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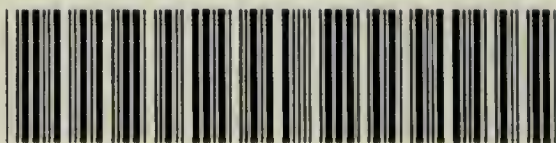   Guide, 1*s*.
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FELLOW OF THE CHEMICAL SOCIETIES OF LONDON AND BERLIN
PROFESSOR OF CHEMISTRY IN THE EAST LONDON TECHNICAL COLLEGE

WITH 63 ILLUSTRATIONS

PREFACE

THIS book was begun about a year ago to meet a want often felt by more advanced organic students. Although several books dealing with the preparation of organic compounds are in existence in the English language, and even more of course in German, very little has been done in the way of giving an account of quantitative organic analysis, methods of molecular weight determinations and a systematic set of organic preparations within the limits of a small book.

Pages 1 to 102 deal with the purification and analysis of substances, and quantitative estimations generally ; the rest of the book being taken up with preparations. An attempt has been made to introduce system in this latter part, and when necessary explanations of the reactions used have been given. It is hoped that this may make the book useful, not only in the mere mechanical skill of preparation and analysis, but also give it a certain educationa value.

<div align="right">J. T. HEWITT.</div>

EAST LONDON TECHNICAL COLLEGE, LONDON, E. :
April 1897.

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PART I

PURIFICATION AND ANALYSIS OF ORGANIC SUBSTANCES

CHAPTER I

THE PURIFICATION OF ORGANIC SUBSTANCES

Crystallisation.—Organic substances, when prepared by any given reaction, are not usually obtained in a chemically pure condition ; reactions very rarely follow a quantitative course, as we find them do when dealing with inorganic materials. Thus, if dilute sulphuric acid be added to a solution of barium chloride, a precipitate is obtained which, after washing and drying, consists of pure barium sulphate if our materials have been pure to start with. On the other hand, suppose that we are carrying out a simple organic reaction, such as the preparation of nitrobenzene by the action of nitric acid on benzene. If the reaction—owing to the use of a too dilute acid—has not gone far enough, we shall find that some of the benzene is left in an unattacked condition. On the other hand, if we obviate this by using a mixture of nitric and sulphuric acids, we are very liable to obtain

considerable quantities of metadinitrobenzene, unless we carefully cool the mixture during the reaction. Consequently, when we pour the mixture into water and obtain mononitrobenzene as a heavy yellow oil, we may be sure that it will contain small quantities of impurities, and, after a careful drying, we shall have to purify our product by a careful distillation, keeping only that portion which distils over within a degree or two of the true boiling-point of the compound.

The methods most frequently used by chemists for obtaining a substance in a chemically pure condition are :

(*a*) Recrystallisation.
(*b*) Distillation.
(*c*) Sublimation.

In the process of recrystallisation the solvents most generally employed are water, ether, alcohol, benzene, petroleum spirit (ligroin), glacial acetic acid, acetone, and chloroform ; sometimes toluene or xylene, nitrobenzene or aniline, are employed. Generally speaking, the finely-powdered substance is added in small quantities to a quantity of the boiling solvent, insufficient to bring the whole into solution. When saturation is approximately attained, more of the solvent is added ; and then, when the liquid has again been brought to boiling-point, more of the substance to be recrystallised is added, the process of adding more of the solvent and substance being repeated until one obtains a boiling nearly saturated solution of the whole of the substance to be recrystallised. The solution is then poured as rapidly as possible through a plaited filter con-
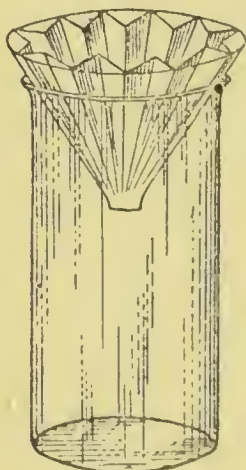
Fig. 1.

tained in a funnel from which the neck has been cut off, and standing, as represented in fig. 1, over a beaker. The arrangement shown is better than that of the usual filter-stand and long-necked funnel, since the latter is apt to be choked by the separation of crystals in the neck during the process of filtration.

After the whole of the solution has been filtered, the contents of the beaker are once more brought to the boiling-point, so that the whole of the substance is brought into solution; the beaker is covered with a clock-glass, and the whole allowed to cool slowly without being disturbed. It is only by slow cooling without stirring that large crystals can be obtained. Agitation usually results in the substance coming down in such a condition that it forms but very small crystals, and in certain cases so finely divided that a crystalline structure cannot be observed.

The so-called crystallising dishes, though useful when crystallisation by evaporation must be resorted to, are not to be recommended in most cases. Beakers are far pre-ferable, as there is far less chance of the liquid creeping over the edge.

Recrystallisation of Sulphanilic Acid from Water. (Paraamidobenzenesulphonic acid, $1:4C_6H_4(NH_2)(SO_3H)$).—Raise 40 c.cm. of distilled water to boiling-point in a beaker of 100 c.cm. capacity, and then add, in small portions at a time, 5 grams of powdered sulphanilic acid. The acid will not be entirely dissolved by the amount of water in the beaker, so gradually add hot water until all the acid is in solution, keeping the contents of the beaker boiling the whole time. Filter rapidly into another beaker of about 150 to 200 c.cm. capacity (see fig. 1), raise the filtrate to the boiling-point, cover the beaker with a clock-glass, and allow to cool slowly. The sulphanilic acid will

separate out in colourless shining prisms, which may be separated from the mother liquor by filtration with a filter pump. The crystals should be washed two or three times with a little cold water, and then dried in a desiccator over sulphuric acid. Weigh the amount of dried re-crystallised sulphanilic acid obtained.

In setting up the filtering apparatus, choose an india-rubber stopper which fits the filter bottle well; or use a sound ordinary cork, which should be squeezed in order to soften it. Then bore one hole for the neck of the funnel, and fix cork and funnel in place. Next take the filter disc (*B*, fig. 2) and cut two circular discs of filter-paper of about 3 mm. greater dia-meter than the porce-lain disc. Place the porcelain disc horizon-tally in the funnel, lay the two discs of filter-paper on it, press down the paper, then mois-ten with water, press again, and see that the paper—the necessarily creased edges of which
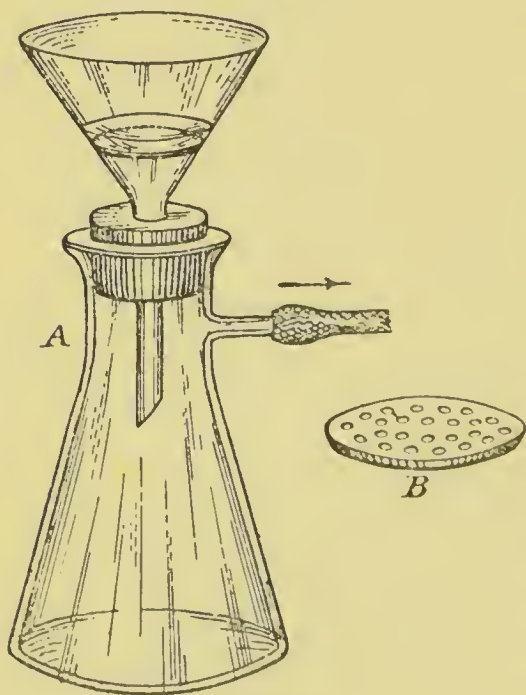
FIG. 2.

are turned upwards—makes such a tight join between the funnel and disc that all liquid poured into the funnel must pass through the paper on its way to the filter-bottle. The tubulus of the filter-bottle is then to be connected by stout-walled india-rubber tubing to a filter-

pump worked by the water pressure of the laboratory.   An efficient form of such pump made in glass is shown in fig. 3 ; the opening, A, is connected by strong tubing to the water supply ; B, to the vessel which it is desired to exhaust.

Somewhat more expensive, but at the same time more durable, pumps can be obtained made in brass.

Recrystallisation of Naphtha-lene $(C_{10}H_8)$ from Alcohol.—In a beaker, or Erlenmeyer flask, of 150 c.cm. capacity, heat 50 c.cm. of ordinary spirit to boiling-point by means of a water-bath, and then add 40 grams of naphtha-lene. The naphthalene will readily go into solution ; remove the flame and then pour the hot solution through a plaited filter into a beaker of about the same size as the one in which solution was effected.   Raise the solution again to boiling, and cover with a clock glass ; on cooling, the naphthalene will be deposited as colourless leaflets.   When cool, filter off with the aid of the pump, wash the crystals with a very small quantity of strong spirit, remove the con-tents of the filter-flask to a dry beaker, and further wash the crys-tals, first with a small quantity of

FIG. 3.

a mixture of 1 volume water to 2 volumes spirit, then with a still more dilute alcohol, and finally with water.

Then dry the crystals, and after weighing the amount obtained, determine the melting-point. This should be 79°.

The mother-liquor from the recrystallisation of the naphthalene, and also the strong alcoholic washings, still contain a small quantity of the substance in solution (100 parts of *absolute* alcohol dissolve 5·29 parts of naphthalene at 15°). This may be recovered by raising the solution to a temperature of about 50° to 60,° and gradually adding hot water until a slight disturbance of the liquid is noticed.

FIG. 4.

Then warm until the solution is once more clear, and allow the liquid to cool slowly. The crystals obtained will probably show a slightly lower melting-point than the first crop.
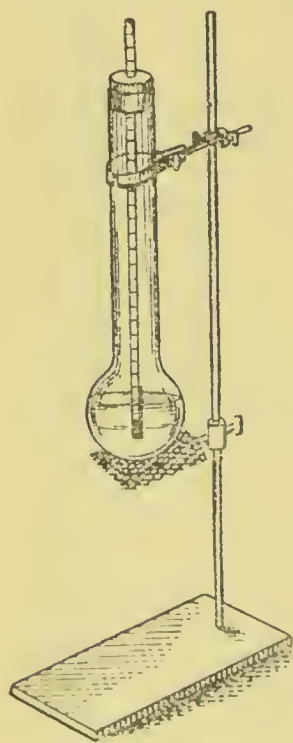
Determination of Melting-points.— Melting-points are determined with the help of the apparatus shown in fig. 4. The bulb of the long-necked small flask is two-thirds filled with strong sulphuric acid; to this a very small crystal of potassium nitrate is added, so that, on heating, oxidation of any impurities present will prevent them discolouring the acid. The thermometer passes tightly through a cork on the side of which a small nick is made, so as to allow the air inside the apparatus to escape as it expands on heating. The substance, the melting-point of which is to be determined, is contained in a small capillary tube closed at its lower end, and attached to the thermometer merely by capillary attraction after moistening with sulphuric acid. The melting-point tubes are made by

heating a piece of pressure tubing—internal diameter about 2 cm.—until fairly soft, and then pulling out steadily but fairly rapidly. If the tube is pulled out too quickly the internal diameter of the capillary tube will be too small to introduce the substance whose melting-point is to be determined with ease; with care, however, one may obtain several feet of serviceable tubing from an inch or two of large diameter tube. When tubes which have been used for the purpose of heating substances under pressure have become too short for use, the remaining ends can be advantageously converted into melting-point tubes. Having obtained a considerable length of capillary tubing, it should be cut into pieces about 6 cm. long, and these sealed at one end by holding for a second or two in a Bunsen flame. The tubes should be kept in a corked specimen tube, or in some other way, so that they shall remain dry and not get contaminated with dust.

When a melting-point is to be determined, one of the melting-point tubes is taken, and by pressing its open end into the finely powdered substance some of the latter is introduced into the tube. The tube is then held vertically, sealed end downwards, and tapped gently on the bench, so that the substance intro-duced falls to the bottom. The process is repeated until enough substance has been introduced to fill 7 or 8 mm. of the sealed end of the tube. The thermometer is now withdrawn from the long-necked flask; the drop of sulphuric acid which ad-heres to it is used to wet the side of the melting-point tube, which can now be attached to the side of the thermometer. Place the melting-point tube

Fig. 5.

in such a way that the substance it contains is on the same level as the thermometer bulb (see fig. 5). The

thermometer and melting-point tube are returned to the
sulphuric-acid bath, which is now heated gradually until
the substance melts ; when this happens observe the tem-
perature.   Always remove the melting-point tube after an
observation ; it is careless to leave the melting-point tube
in the bath after a melting point has been determined.

It need scarcely be added that the accuracy of a
melting-point determination will depend not only on the
skill of the observer but also on the accuracy of the ther-
mometer.   Consequently, the thermometer should either
be compared with a normal instrument, the two thermo-
meters being heated in the same well-stirred bath of
sulphuric acid, or a control may be made by freezing or
boiling-point determination of well-known substances.
For particulars refer to physical handbooks.

Before leaving the subject of recrystallisation, it should
be borne in mind that occasionally a mixture of solvents
gives a better result than one solvent alone.   Thus, in a
case where a substance is extremely soluble in alcohol even
when cold, and, on the other hand, is insoluble in water,
one may sometimes obtain good results by using a mixture
of alcohol and water.   We have already seen in the case
of the recrystallisation of naphthalene from alcohol that
the spirit keeps an appreciable quantity of the hydrocarbon
in solution, even on cooling, and that the greater part of
this residual quantity may be recovered by adding hot
water to the warmed alcoholic solution.   This is an
example of the case in point.   Other examples of mixed
solvents are acetic acid and water, benzene and ligroin,
chloroform and benzene or ligroin.   When mixed solvents
are resorted to, choose, if possible, that the substance
should be more soluble in the solvent of lower boiling-
point, for, if crystallisation by evaporation is resorted to,

the more volatile solvent will escape first. It is easily
seen that, if the more volatile solvent be the one in which
the substance is less easily soluble, the substance is
very likely to be retained in solution as evaporation pro-
ceeds, instead of crystallising out. When possible avoid
crystallisation by evaporation; such avoidance is usually
possible if the right solvent be chosen and be employed in
the right quantity. When crystallisation by evaporation
must be resorted to, it can be carried out in a crystallising
basin; but care must be taken that the contents are pro-
tected from dust, and that the liquid does not creep over
the edge more than can possibly be helped. A crystal-
lising dish should never be covered with filter-paper, it is
far better to support a clock glass over it by means of a
triangle of glass rod.

Distillation.—In the case of substances which are
liquid at ordinary temperatures, purification is usually
effected by distillation in order that substance of a
constant boiling-point may be obtained. Sometimes, how-
ever, one resorts to a freezing-out of a substance from a
liquid mixture; this is, of course, only a case of crystal-
lisation, it is not generally applicable, and is used com-
paratively rarely.

Distillation of Aniline.—Weigh out 100 grams of
commercial aniline and pour it into a boiling-point flask
(*i.e.* a round-bottomed flask provided with a side-tube)
capable of holding about 200 c.cm. Choose a well-fitting
cork, softened by rolling, for the mouth of the flask, bore
one hole through this for the introduction of a thermo-
meter. Take care that, although the hole is a close and
air-tight fit for the thermometer, it is not too small,
as there is always a certain amount of risk in putting a
thermometer through a cork. Next get a Liebig's con-

denser (about 40 to 60 cm. length of water-jacket) and fit the larger end with a cork, through which the side tube of the boiling-point flask must pass. The general arrangement of the apparatus is shown in fig. 6 ; one or two points should be noticed. The distilling-flask is clamped above the side tube, the reason being that the heated vapour is liable to expand the glass below this point, and if the clamp is screwed up tightly the neck of the flask may be broken. Again, in case of an accident happening, the thermometer will probably be saved by having the clamp near the cork. The bulb of the thermometer is arranged so that it is almost on a level with the side tube, if anything a little lower ; it is thus exposed to the temperature of the vapours which enter the condenser. The side tube of the distilling-flask passes through a well-bored cork firmly fixed in the wide end of the condenser ; it should not merely just go through the cork, but project an inch or two into the condenser. The cold water from the tap enters the lower end of the condenser and leaves at the upper end nearer the distilling-flask. Note especially that india-rubber stoppers *must be avoided* ; they will be destroyed by the heat of the aniline vapour, and, moreover, the aniline will exert a certain amount of solvent action on them and so be contaminated. The flask is not supported by wire-gauze ; this may be necessary when one is distilling a large quantity of a liquid on account of the weight, or if a liquid of low boiling-point is being dealt with.

Having the apparatus arranged in the way described, we must now get ready a clean beaker and a clean and perfectly dry stoppered bottle for receiving the aniline. Placing the beaker to receive the first distillate, the operation may be started by gradually heating the flask and its
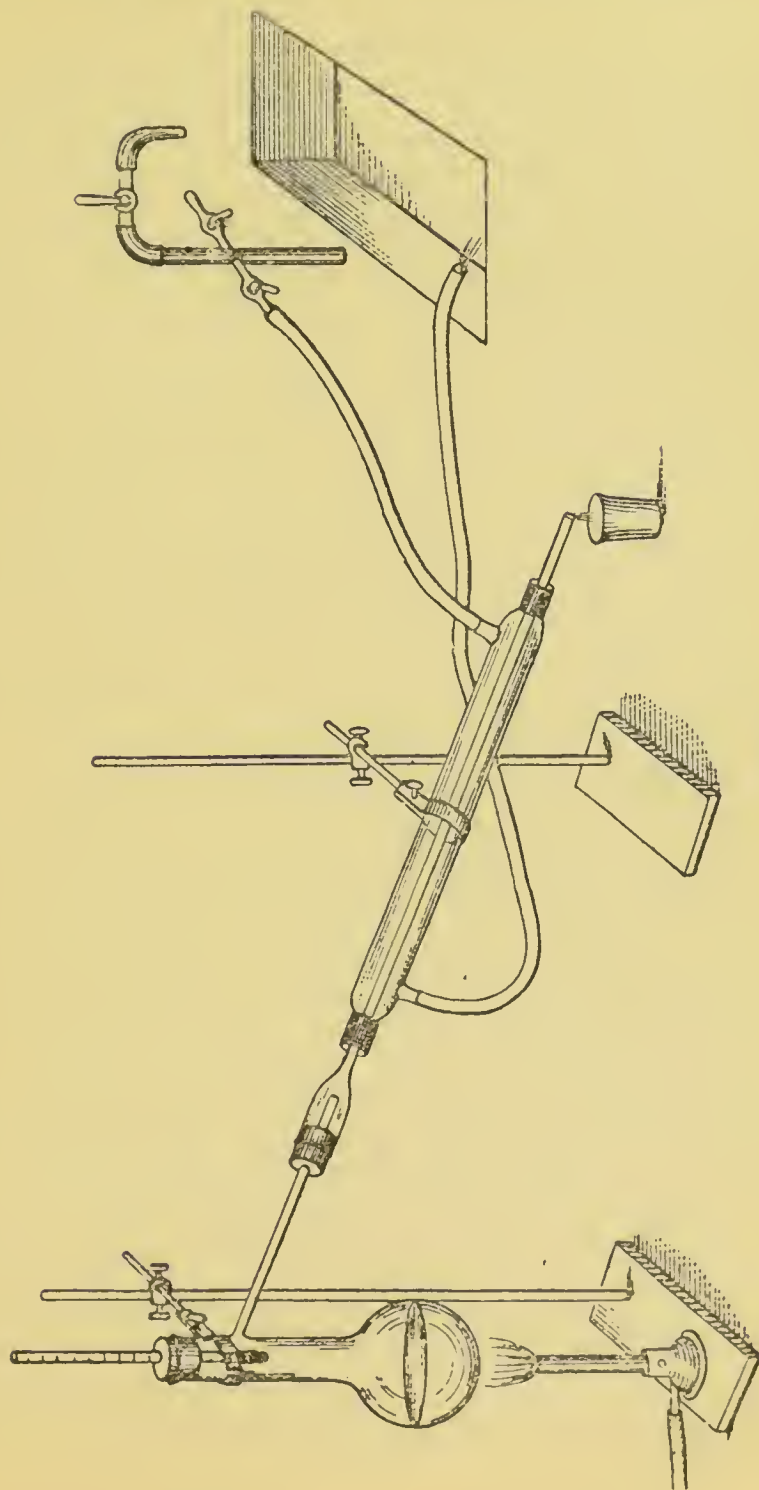
FIG. 6.

contents by a clear Bunsen flame of not too great a size. The first liquid will come over about 100° ; the aniline is sure to contain a small quantity of water. The steam will naturally carry a small quantity of the aniline with it, the result being that the distillate is milky. In dealing with a large quantity of aniline it would be worth while to refractionate these first runnings. Very soon, however, the thermometer will rise somewhat suddenly to 184° (if the barometric pressure is 760 mm.). As soon as the liquid comes away clear from the end of the condenser, remove the small beaker and replace it by the well-dried bottle, which has previously been weighed. All that distils between 182° and 186° may be collected ; the bottle and its contents should be weighed again. From the 100 grams of aniline at least 85 to 90 grams should distil within a degree or two of 184°. Note the temperature at which the major portion passes over.

In conducting a distillation in this way it is very probable that the thermometer will register a degree or two less than the true boiling-point. This is to be expected, as it is obvious that the whole of the column of mercury will not be at the same temperature as the mercury in the bulb. Thermometers are, however, made which only begin to register temperatures much above the ordinary ; for instance, the 100° mark may be close to the bulb. With such a thermometer it is easy to arrange the apparatus in such a way that the whole of the mercury column is in the vapour given off from the liquid. If, however, it is impossible to have the whole thread of mercury in the vapour, the boiling-point may nevertheless be corrected. Suppose, for instance, that the length of thread of mercury which is not directly heated by the vapour extends over a length equal to x degrees of the thermometer scale ; the mean

temperature of this portion is determined by observing the temperature registered by another thermometer in the middle part of the length x.   Since the apparent coefficient of expansion of mercury in glass, *i.e.* the differences in the coefficients of expansion of mercury and glass, is about ·00016, it is obvious that we must add to the observed boiling-point a quantity represented by $0.00016\ x\ (t-t')$ where t and t' respectively represent the observed boiling-point and the mean temperature of the portion of the thread not directly heated by the vapour. In all cases the barometer should be read and noted when a boiling-point is determined.

Fractional Distillation.—In the case we have just examined we have had to deal with one liquid mixed with only a slight amount of impurity, and have not endeavoured to resolve a mixture of two or more substances into its constituent parts.   The problem is in this case much more complicated, since we find that we get a perfectly gradual change of boiling-point in most cases. Thus, if we mix equal volumes of alcohol and water and then distil, we find that, although alcohol predominates in the first portion of the distillate and water in the second, we by no means get even an approximate separation of the mixture into its two constituents by one distillation.   The alcoholic portion will contain a considerable quantity of water, and the water a certain amount of alcohol.   Nevertheless, a mixture of liquids may generally be very nearly separated into its constituents, or, in some cases, almost perfectly, if only we repeat the process of fractional distillation several times.

Separation of Acetic Acid and Ethyl Acetate.—Set up apparatus for distillation such as is represented in fig. 6, but choose a distilling flask in which the distance between

the bulb and side tube is fairly long—not less than 10 cm.
Now pour into the flask a mixture of 50 grams of ethyl
acetate and 50 grams of glacial acetic acid ; the first of
these substances boils at 78°, the second at 118°. Before
starting the distillation see that you are provided with
several small, clean, and perfectly dry beakers, and also
with a somewhat smaller clean dry boiling-point flask
capable of holding about 100 c.cm. Now start the
distillation, taking care that distillation is not too rapid.
Collect all that passes over between 78° and 90° in one of
the small beakers. When the latter temperature is reached,
change the receiver and make a second fraction of what
passes over between 90° and 105°. Now change the receiver
again, and collect as the third fraction all that passes over
from 105° to 118°. The contents of the beakers, as they
are removed from the end of the condenser, should be pro-
tected by being covered with small clock glasses.

Using now the second smaller distilling flask, we begin
a second fractionation, by pouring the first fraction into it
and cleaning the beaker in which it was contained, so as
to be able to use this beaker for collecting the first frac-
tion of the second distillation. During this second distilla-
tion, all that passes over up to 90° is collected in the first
beaker, the distillation is then stopped, whilst the second
fraction of the first distillation is added to the contents of
the boiling-point flask. On resuming the distillation it
will be found that there is still a certain amount which
comes over before 90° ; this must go into the first beaker.
At 90° receivers are changed, the fraction from 90° to 105°
being collected in the same beaker that was used for the
corresponding fraction of the first distillation ; this beaker
need not be cleaned between the two distillations. When
105° is reached, the contents of the third beaker are poured

into the distilling flask, and on resuming the heating it will be found that there are small quantities to add to the first and second fractions; the third fraction will, as before, be collected between 105° and 118°. After this second distillation it will be found that the fraction from 90° to 105° is much smaller than it was after only one distillation, a considerable portion having passed into the first and last fractions. By a few repetitions of the process, the second fraction will be found to become almost negligeable in quantity; these two end fractions are then each of them distilled separately; that portion of the first fraction which distils up to 79° may be taken to be almost pure ethyl acetate, whilst that amount of the end fraction which distils above 116° may be collected as acetic acid. With the quantities taken, about 30 grams of ethyl acetate and somewhat more acetic acid should be recovered.

In certain cases it is advisable, in order to avoid decomposition, to distil a substance under reduced pressure. The manner in which this is carried out will be described later on.

Sublimation.—Occasionally substances are purified by the process known as sublimation; their heated vapours are somewhat quickly cooled, so that they are deposited in a solid crystalline condition without passing through an intermediate liquid stage.

Sublimation of Benzoic Acid.— Weigh out 2 grams of benzoic acid on to a clock glass of at least 10 cm. diameter, over this place a piece of filter paper, through which several holes have been made. Cover the
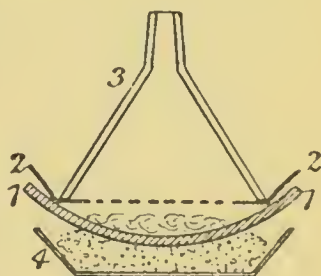
Fig. 7.

whole over with a funnel, smaller than the clock glass in diameter. In fig. 7, 1 1 represents clock glass, 2 2 the

filter paper, and 3 the funnel, whilst 4 is a small sand
bath on which the clock glass is placed and through which
a steady heating is effected.   The object of the filter
paper is to retain sublimed benzoic acid, which becomes
detached from the sides of the funnel, from falling back
into the clock glass, the holes being to allow the vapour to
pass upwards.

CHAPTER II

THE ULTIMATE ANALYSIS OF ORGANIC COMPOUNDS

Qualitative Detection of Elements.—Before proceeding to an elementary quantitative analysis of an unknown organic compound it is necessary to know what elements are present. The processes for detecting these differ very materially from the processes in use in inorganic work.

Carbon and **Hydrogen** are, of course, almost always present in organic substances, and the presence of the former can, in the majority of cases, be detected by heating some of the substance alone in a dry test-tube. Charring takes place as a general rule, and if water or hydrocarbon vapours are evolved, it necessarily follows that hydrogen is also present. Some substances are, however, volatile without decomposition on heating, in which case the rough dry distillation test is of course quite useless. A generally applicable method is to heat some of the substance with dry, freshly ignited powdered copper oxide in a hard glass tube, 7 to 10 cm. in length, which may be provided with cork and leading tube. The deposition of drops of water on the cooler part of the tube in which heating is effected, and also in the leading tube, gives evidence of the presence of hydrogen, whilst by leading the escaping gases through lime-water, the carbon dioxide which is also formed may be readily detected. Try this reaction in the case of cane-sugar, oxalic acid, and sulphanilic acid, using ·1 to ·2 gram substance, and 2 or 3 grams of copper oxide.

C

Nitrogen is detected with greatest certainty by con-
verting it into sodium cyanide, which is then used for
making Prussian blue. Heat a few flakes of acetanilide in
a glass tube about 5 mm. diameter and 5 cm. in length,
with a piece of sodium about the size of a mustard seed.
Continue the heating until the excess of sodium has been
volatilised, then cool and add a few drops of water. If
the sodium has not been entirely used or volatilised, a
rather violent reaction may take place; caution should
always be exercised, and never take too much sodium in
the first instance. A couple of drops of ferrous sulphate
solution should now be added, one of ferric chloride, then
a few drops of caustic soda solution. Warm gently, and
finally acidify the contents of the tube with hydrochloric
acid. A residue of Prussian blue shows the presence of
nitrogen in the acetanilide.

The sodium has combined with the nitrogen and
some of the carbon of the acetanilide, producing sodium
cyanide, which reacts with ferrous sulphate to form sodium
ferrocyanide.

$$6NaCN + FeSO_4 = Na_2SO_4 + Na_4Fe(CN)_6.$$

Sodium ferrocyanide and ferric chloride give ferric ferro-
cyanide (Prussian blue).

$$3Na_4Fe(CN)_6 + 4FeCl_3 = 12NaCl + Fe_4'''[Fe(CN)_6]_3^{iv}.$$
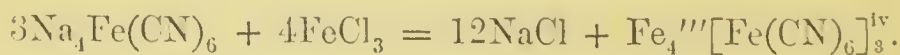
Organic substances which contain both nitrogen and
sulphur yield a thiocyanate on heating with sodium; if,
however, iron-powder is added, a cyanide is nevertheless
produced, the sulphur uniting with the iron. Test for
nitrogen in sulphanilic acid proceeding in the same way
as with acetanilide. only before heating with sodium mix
with a pinch of reduced iron.

The Halogens.—Chlorine, bromine, and iodine cannot be detected in the same way in organic compounds as in ordinary salts.   Add a drop or two of ethyl bromide to a silver nitrate solution; no precipitate of silver bromide is produced.   Metallic bromides, on the other hand, give, as is well known, an immediate yellowish-white precipitate of silver bromide; in the latter case the salt is electro-lytically dissociated in aqueous solution, and the reactions of its ions are easily enough observed.   On the other hand, the halogen in such a substance as ethyl bromide is intimately bound in the molecule, and electrolytic dis-sociation does not take place in solution.   To show the presence of a halogen element in an organic compound, the simplest way is to hold a piece of copper oxide sup-ported at the end of a platinum wire in the edge of a Bunsen flame until no green colour is communicated to the flame.   On dipping the still warm copper oxide into any halogen compound, and again heating it in the outer Bunsen flame, it is found that the latter is tinged green. It is only the halogen compounds of copper which com-municate a green colour to the flame, and for this test the compound may be either inorganic or organic.   The test may be tried with chlorobenzene, bromobenzene, and iodbenzene; the same green colour is observed in each case.   Obviously, we should not be able by this test to differentiate as to which halogen is present; if this were necessary—and usually it is not, since under the circum-stances by which any compound is formed we know which halogen *can* be present—it would be necessary to destroy the organic matter and obtain the halogen as a metallic salt.   This is most easily done by ignition with quicklime (see first that the lime is itself free from halogen salts); by treatment of the residue with dilute nitric acid, a

solution will be obtained in which the halogen can be detected by the ordinary qualitative tests.

Sulphur.—The simplest way of detecting this element is to heat some of the substance to redness in a small specimen tube with a small piece of sodium, by which means sodium sulphide is obtained. On adding dilute acid to the residue left in the tube, sulphuretted hydrogen is naturally evolved, which may be detected either by its smell or its action upon filter-paper moistened with a solution of lead acetate.

Phosphorus is detected by heating with magnesium-filings in a small specimen tube, whereby magnesium phosphide is produced. After cooling, this is decomposed with evolution of phosphoretted hydrogen by the addition of water ; the gas is readily recognised by its smell.

The Metals, when combined with organic acids, may frequently be directly detected by the usual qualitative tests, but since some of the organic acids hinder precipitation with ammonia in the third group, and in any case strongly coloured organic substances are liable to mask a good many reactions, it is better to destroy organic matter before starting a qualitative examination for metals. either by a simple ignition, or by heating strongly with acid potassium sulphate. It need scarcely be added that it is no use looking for mercury after this treatment ; it should either be detected in the dry way or precipitated by sulphuretted hydrogen from a solution of some of the un-ignited substance.

Quantitative Analysis of Organic Compounds.—In performing the quantitative estimation of one or more constituents of an organic substance, even greater care is requisite than in dealing with inorganic substances, since one rarely wishes to use more than 2 decigrams for

the purpose of an estimation, and in many cases, even when one has plenty of substance at one's command, it is extremely inconvenient to take more.

Estimation of Carbon and Hydrogen.—We shall first take the estimation of carbon and hydrogen in compounds which contain only these two elements, or perhaps oxygen in addition. This is carried out by the process of combustion ; a weighed quantity of the substance is heated in a current of oxygen, the water formed is collected in a drying-tube charged with calcium chloride, and the carbon dioxide in a bulb apparatus containing a 50 per cent. solution of caustic potash. For the purpose of heating the tube in which combustion takes place, a furnace about 30 inches in length is required, with about thirty burners, either of the ordinary Bunsen pattern, or perhaps with narrow, elongated tops, so as to give a more nearly continuous flame under the trough in which the combustion tube is heated. The author prefers a plain Erlenmeyer pattern of furnace, *without* any arrangement for lowering or raising the whole of the burners during the progress of a combustion.

The analyst will require the following apparatus, besides the combustion furnace and necessary balance for carrying out such analyses :—

1. Two gasholders, one containing oxygen, the other for air.

2. A drying apparatus made in duplicate, so that one can use one half for drying air, the other half for oxygen.

3. A combustion tube of hard glass, open at both ends, of about 15 mm. external diameter ; it should be of such a length as to overhang the trough of the furnace in which it is laid by 3 or 4 cm. at either end. This tube needs to be supplied with an india-rubber stopper at either

end.   These stoppers must be of good quality, and each bored with one small hole.

4. About 400 to 500 grams of coarse copper oxide.

5. Copper gauze and copper wire for making spirals.

6. A porcelain boat, together with a glass tube case for keeping it clean.

7. A desiccator and clock glasses.

8. A U-shaped calcium chloride tube.

9. Potash bulbs of Geissler's pattern.   These should possess a short calcium chloride tube.

10. Sound india-rubber connection tubing.

11. Glass rod.

Gasholders are almost always supplied to each combustion furnace, and very frequently drying apparatus as well.   A convenient form of drying apparatus, which occupies only a small space and works very efficiently, is represented in fig. 8. A, A^1 represent wash-bottles containing strong sulphuric acid, B, B^1 are towers filled with pieces of stick potash about 3 cm. in length. $C C C$ is a U-tube, represented on a larger scale in fig. 9.   This contains a small quantity of sulphuric acid in its lower portion ; the rate at which air or oxygen bubbles through this offers a good idea of the rate at
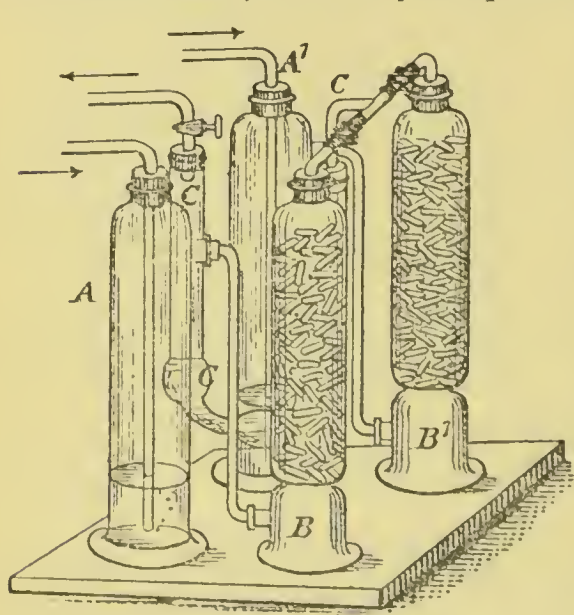
FIG. 8.

which the gas in question is travelling through the apparatus. One sulphuric acid wash-bottle and tower serve for purifying oxygen, the other pair for air. The reason these are made in duplicate is that when air is substituted for oxygen at the end of a combustion, no time is wasted in replacing the whole of the oxygen in the drying apparatus by air. It is only necessary to replace the oxygen in the tube *C*, in the combustion tube, calcium chloride tube, and potash bulbs.
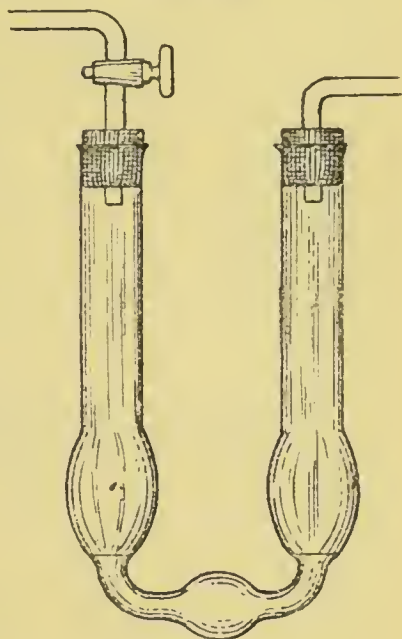
Fig. 9.

The Combustion Tube.—We shall suppose the length of the trough of the furnace to be 75 cm. Cut a length of 83 or 85 cm. from a good piece of combustion tubing of about 15 mm. external diameter. Jena glass is preferable to the ordinary combustion tubing. It is extremely hard to cut and round at the ends, but has the advantage that it will stand the high temperature of the combustion furnace admirably, so that 12 to 20 combustions may frequently be carried out in the same tube. When a convenient length of tube has been cut, the ends must be rounded off by heating in the blowpipe flame, and may with advantage be slightly opened out with a conical piece of charcoal. One must, however, be careful that this opening is not too great. When the ends are cold, the tube should be carefully dusted inside and out. It is not of much use to clean it with potassium dichromate

and sulphuric acid, since when prepared it has in any case to be heated for some time to a low red heat whilst a current of oxygen is passed through, so that any organic
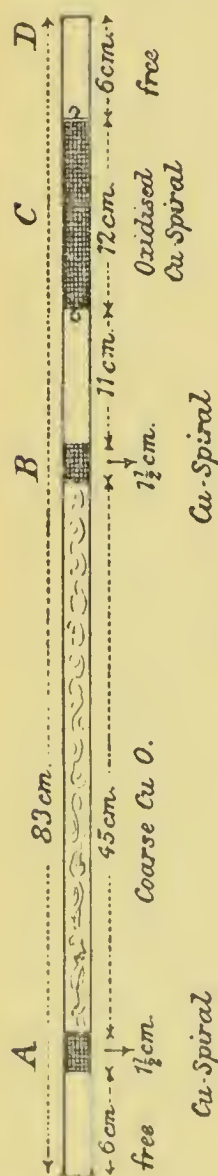
Fig. 10.

matter may be oxidised and got rid of. A length of about 45 cm. of the tube is packed with coarse copper oxide, held in place by copper spirals. The coarse copper oxide may either be bought or made by the experimenter; in the latter case stout copper wire is cut up into lengths of 6 to 10 mm., and heated to bright redness for some hours in a muffle furnace, with free access of air. The same process can also be carried out with copper turnings. Good copper oxide can be obtained in this way at a cheap rate. After ignition the copper oxide should be put whilst still warm into glass flasks provided with sound india-rubber stoppers and calcium chloride tubes. The copper spirals intended to hold the copper oxide in place in the tube are made by cutting two strips of copper gauze, 10 cm. by $1\frac{1}{2}$ cm., which are rolled up in such a manner that the spirals formed just fit the tube tightly. The spiral A is then fixed in the tube with the help of a glass rod, copper oxide is filled in for a length of 45 cm., and the spiral B is put in position also by the help of glass rods. The spiral C, which needs to be thickly coated with copper oxide, is made by winding a piece of copper gauze

measuring 10 cm. by 12 cm. round a stout piece of copper wire about 14 cm. in length; the two projecting pieces of wire are then bent round into eyes, so that the spiral can easily be withdrawn from the tube by a hook made of a similar piece of copper wire. Spiral and hook are shown in fig. 11. In making the spiral remember that it has to be withdrawn frequently from the tube, which it must not fit too tightly. The tube, with spiral C in its proper position, is now placed in the furnace, each end of the tube being supplied with a good one-holed india-rubber stopper. The end, C, of the tube is connected with the drying apparatus by means of a piece of glass tubing passed through the stopper and sound india-rubber connection

FIG. 11.

tubing. The tiles of the furnace are laid back so as not to close in on the tube, and all the burners of the furnace are lighted, but in such a way that their flames do not come at all above the trough. After ten minutes the tiles may be closed in, and a few minutes later the burners may be slightly turned up. In this way the tube and its contents are soon raised to dull redness; meanwhile a steady, slow stream of oxygen is led through the apparatus. When oxygen can be detected at the other end of the tube (near spiral A) the roasting process is complete, the burners from B to D are to be turned out, and this end of the tube is allowed to cool, whilst the oxygen is cut off, and a slow stream of air passed through in its place. The india-rubber stopper at A should be fitted with a short straight calcium-chloride tube and put in its place in the tube until the experimenter is ready to begin his combustion.

Calcium-Chloride Tube and Potash Bulbs.—One of the best forms of calcium-chloride tube is shown in figs. 12 and 13; the former represents the apparatus empty, the latter as fitted up ready for use. The tube is first carefully cleaned, using in succession caustic-soda solution, water, potassium dichromate, and sulphuric acid, and finally distilled water. It is then carefully dried by gently warming and drawing through the tube a current of air, very conveniently by means of a filter pump.
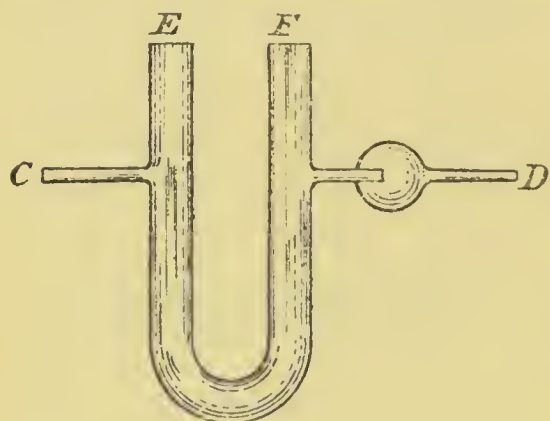
FIG. 12.

Two stoppers are made to fit on the ends of the side tubes. For this purpose two pieces of well-fitting connection tube, each about 2 cm. in length, and provided with a piece of glass rod 15 mm. long, and rounded off neatly at the ends, are necessary. The tube can now be filled with dry granular calcium chloride
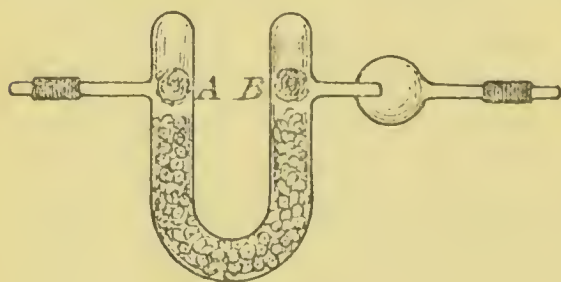
FIG. 13.

nearly up to the level of the side tubes, plugs of glass wool, A and B, being then introduced. To seal off the ends one of the stoppers is slipped over C, and E is closed with a tightly-fitting cork. The glass at F is now softened in the blowpipe flame, drawn out, the seal strongly heated and

rounded by gently blowing through D.   The cork is now re-
moved from E, and F being already hermetically closed, E
may similarly be sealed off.   When drawing off the ends E
and F do not leave the ends too short, otherwise the glass
wool at A and B may be fused.   Moreover, there is a
greater chance of cracking where the T-joints are situated.
Another reason for leaving the ends moderately long is
that when the calcium chloride in the U-tube is used up,
the tube may be refilled and used again if a sufficient
space has been left for a new seal.   Since the calcium
chloride frequently contains small quantities of lime, it is
necessary that the latter should be converted into calcium
carbonate before the tube is used, otherwise the results
obtained on analysis will show a deficiency in carbon,
whilst the numbers for hydrogen will be too high, owing
to some of the carbon dioxide being weighed with the
water.   To saturate the calcium chloride with carbon
dioxide, a Kipp's apparatus, containing marble and hydro-
chloric acid, is connected with a washing bottle holding
sulphuric acid; the dried gas is passed from this in a slow
stream through the calcium-chloride tube for about twenty
minutes.   The tube is then disconnected, closed by means
of its stoppers, and allowed to remain in this condition for
some hours.   This operation may be advantageously per-
formed overnight.   In the morning
the stoppers are removed, and the
excess of carbon dioxide displaced
by drawing a current of air through
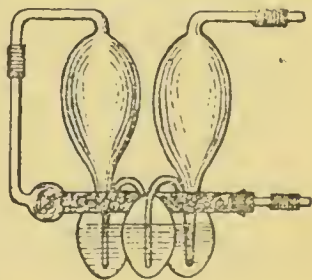the apparatus.   The stoppers must
then be put on again.

FIG. 14.

The most convenient potash
apparatus is of Geissler's bulb pat-
tern, represented in fig. 14.   This consists of two

larger bulbs at the top and three smaller ones below,
through which the gases, after leaving the calcium-chloride
tube, have to pass in succession. Carbon dioxide absorp-
tion is effected by filling these smaller bulbs two-thirds
full with a strong solution of caustic potash (made by
dissolving stick caustic potash in an equal weight of
water). This is done by disconnecting the calcium
chloride tube, which in the figure is shown in position,
attaching a piece of india-rubber tubing to one end of the
apparatus and carefully sucking up the potash solution
contained in a small basin through the other end. Great
care is necessary that none of the potash enters the mouth.
The drying tube is filled with granulated calcium chloride
between glass-wool plugs, the open end being closed with

Glass India-rubber Glass

Fig. 15.

an india-rubber stopper through
which a short piece of glass tube
passes, the other end being con-
nected with the potash bulbs by a
short piece of india-rubber tubing.
In making the joint see that the two ends of glass tubing
are in contact. All joints made in organic analysis should
be like that shown in fig. 15. The two ends of the potash
apparatus must now be provided with stoppers similar to
those described for the calcium chloride tube.

In some forms of Geissler's apparatus the drying tube,
instead of lying between the bulbs, as shown in fig. 14, is
attached to the tube of the last bulb by a ground-glass
stopper, and lies at a higher level than the bulbs. Such
potash bulbs have the disadvantage that they are unsteady
on account of the high centre of gravity and the small
base offered by the three lower bulbs. Liebig's pattern
of bulbs is somewhat antiquated and now but rarely used.

The boat in which the substance to be analysed is

placed is made of platinum or porcelain. The latter
answers almost all purposes, and has the advantage that
on account of its whiteness the analyst can readily see
whether all the carbon is burnt off or not. If the boat is
stained, boil it for a few minutes in a test-tube with
nitric acid, then wash it well with distilled water, and
holding it by a pair of tongs heat it to redness in the
blowpipe flame. Allow the boat to cool somewhat, but
whilst still warm place it in the boat-case made by cutting
off two test-tubes which fit one another fairly well, the
outer one being laid in a groove cut in a fairly large flat
cork. Boat and boat case are now
allowed to cool thoroughly in a de-
siccator before weighing.
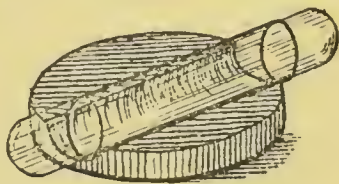
Analysis of Cane Sugar.—All
the apparatus being ready, and the
combustion-tube thoroughly roasted,
we can   proceed with analysis.

Fig. 16.

Finely powder $\frac{1}{2}$ gram of pure cane sugar in an agate
mortar, spread it on a watch-glass, and allow it to
dry in a desiccator over sulphuric acid for some hours.
A vacuum desiccator can be used here with advantage,
and the substance may be placed in it overnight if
an analysis is to be made in the morning. The cal-
cium-chloride tube and potash bulbs, which have been
some time in the balance case so as to acquire its tempera-
ture, are now weighed, the stoppers being first removed.
It is advisable to weigh without the stoppers, since they
may very readily be put on the wrong pieces of apparatus.
The ignited, cooled, and desiccated boat is now weighed
empty, and then ·15 to ·2 gram of substance is carefully
introduced into it from the watch-glass by means of a
small spatula. The boat and its contents are accurately

weighed, the difference in the two weighings giving the amount of substance taken. The boat and its case are now returned to the desiccator, whilst the calcium-chloride tube and potash bulbs are attached to the combustion-tube. We suppose that a slow current of air from the drying apparatus is passing through the combustion-tube, which is at a dull red heat from A to B and cold from B to D (fig. 10). The short calcium-chloride tube is removed from the india-rubber stopper at A, and the weighed calcium-chloride tube substituted in its place, so that the end on which the bulb is blown is nearest to the furnace. To the other end of the calcium-chloride tube the potash bulbs are attached by means of a sound piece of india-rubber tubing at least 3 cm. long, the two glass tubes making a butt-joint, as in fig. 15. The potash bulbs are supported on a stand, the calcium-chloride tube may be held up by props or hung from hooks on an overhead frame, though really no support beyond the rubber stopper in the combustion tube on the one side and the potash bulbs on the other is necessary. The stopper is removed from the end of the drying tube of the potash bulbs and replaced by a piece of india-rubber tubing about 10 to 15 cm. in length. All the joints of the apparatus being apparently tight, they are tested in the following manner :—The glass stopcock between the U-tube of the drying apparatus and the combustion-tube is shut, and with the help of the india-rubber tube at the end of the potash bulbs air is sucked out of the whole apparatus. On removing the mouth, air runs back to restore the pressure in the combustion apparatus to equilibrium with the atmosphere, and in this way a certain amount of the potash solution is forced into the large bulb nearest to the calcium-chloride tube. If the joints are all air-tight, the level of the solu-

tion in the last bulb will not be appreciably altered after several minutes. To see whether any motion of liquid does take place, it is best to observe the solution in the narrow tubes joining the small bulbs of the potash apparatus. The apparatus proving itself to be perfectly airtight, the india-rubber stopper at D (fig. 10) is removed, the oxidised copper spiral caught with the copper wire hook and pulled out; it must be removed from the tube by means of tongs, and on *no account* touched with the fingers. The boat and its contents are now brought into the tube from the boat-case; this can be done without the use of the fingers by slightly tilting the tube in which the boat lies, and then gently tapping it. The boat and its contents are now pushed forward nearly to B (fig. 10) by the copper hook, the oxidised spiral replaced in its proper position, and the india-rubber stopper, with its tube from the drying apparatus, replaced in position. The air supply is shut off, and oxygen sent through the apparatus at such a rate that about one bubble per second comes through the potash bulbs. The burners under C are lighted, and as soon as possible the tiles at C are closed over the tube, so as to raise the oxidised spiral to dull redness as quickly as is compatible with safety. After fifteen minutes one begins to light the burners under the boat, starting from C and working gradually to B. On no account turn up the burners too rapidly, or the result will be that the sugar will be dry-distilled; and though the vapours coming off cannot fail to be burnt by the hot copper oxide, yet a mass of hard carbon will be formed, since all cannot be burnt so rapidly by the oxygen stream, the result being that great difficulty will afterwards be experienced in burning this mass of carbon away. The time occupied in burning a substance will vary largely with its nature and also

with the amount used. Care must be taken in the case
of volatile substances, or with those that readily give off
volatile vapours, in not heating too rapidly, otherwise there
will be a great rush of gas which cannot be properly
absorbed by the chloride of calcium tube or potash appa-
ratus, whilst in certain cases one may even have an
explosion, with the result that not only will the analysis
be useless, but that the back rush of gases will damage the
drying apparatus. It is better to proceed too slowly than
too quickly, especially in the case of the first few analyses.
After thirty to forty minutes from the time of beginning
to light the burners under the boat, the whole of the sugar
will be burnt off. It will be observed in most cases that
but a very small quantity of gas passes through the potash
bulbs, the oxygen now being used to reoxidise the
metallic copper formed in the neighbourhood of B by the
reduction of the copper oxide by the vapours from the
sugar. During this stage the supply of oxygen may be
somewhat increased ; when the reoxidation is complete
the oxygen will begin to issue at the end of the potash
apparatus, and should be detected by a glowing splinter.
As soon as a splinter will easily burst into flame when
brought into the issuing gas, it is a sign that the combus-
tion is complete. The oxygen supply is then cut off and
replaced by a current of air from the other gasholder, this
being continued until oxygen can no longer be detected
by means of a glowing splinter. During this stage the
experimenter should see if any drops of water have
collected in the portion of the tube between A and the
stopper by means of which the calcium-chloride tube is
affixed. If so, it should be chased into the calcium chloride
tube by gently warming this portion of the tube either by
a hot tile or preferably by a Bunsen burner or small spirit-

lamp. Due care must be exercised during this operation that the india-rubber stopper is in no way damaged by the heating ; in fact, during the whole of the combustion great care must be taken in this respect. The stoppers can be well protected by slipping over the ends of the tube sheets of asbestos cardboard in which circular holes have been cut.

The calcium-chloride tube and potash bulbs are now detached, their stoppers put on and placed in the balance case, where they must be left at least thirty minutes before weighing, so that they can be weighed under the same conditions of temperature as before the analysis.

Whilst these are cooling, the combustion-tube needs attention. If it is desired to make another combustion immediately, the short calcium-chloride tube is inserted, and the burners from B to D (fig. 10) turned out, whilst those from A to B are turned down slightly. If, on the other hand, the tube is done with for the day, all the burners are turned out, and the tube is allowed to cool slowly, the short calcium-chloride tube being inserted at the end A. When cold, the two india-rubber stoppers are removed, two tightly-fitting corks inserted, and the tube removed from the furnace until again required.

When the calcium-chloride tube and potash bulbs are weighed, the result of the analysis can be calculated. Results can be entered in the following way :—

Weight of boat and substance	5·3151
Weight of boat	5·1448
Cane sugar taken	·1706
Weight of potash bulbs (after)	56·0637
Weight of potash bulbs (before)	55·8002
Carbon dioxide formed	·2635

D

Weight of calcium chloride tube (after)   .   .   . 41·7558
Weight of calcium chloride tube (before) .   .   . 41·6565

Water formed   .   .   .   ·0993

$$\text{Found} \begin{cases} \dfrac{\cdot 2635 \times 3 \times 100}{\cdot 1706 \times 11} = 42 \cdot 12 \ \% \ \text{C}. & \text{Calculated} \begin{cases} 42 \cdot 11 \\ \\ 6 \cdot 43 \end{cases} \\ \dfrac{\cdot 0993 \times 100}{\cdot 1706 \times 9} = 6 \cdot 47 \ \% \ \text{H}. \end{cases}$$

The calcium-chloride tube can be used for a number of analyses without recharging; this is needed as soon as signs of deliquescence in the end nearest the furnace are visible. The potash bulbs should be refilled every two or three combustions, according to the quantity of potash solution they contain.

The student should now make further analyses of substances containing only carbon and hydrogen (or oxygen in addition). Take in succession salicylic acid, benzoic acid, and naphthalene. As these are rather volatile, much care must be taken.

Very difficultly volatile liquids may be analysed by direct weighing into the boat; but should the liquid be volatile without decomposition, it is preferable to enclose it in a small glass bulb at the end of a capillary tube.

FIG. 17.

Such a bulb is first weighed empty, and the liquid then filled into it by warming the bulb and dipping the open end of the capillary under the surface of the liquid. As the air in the bulb cools, the atmospheric pressure forces in some of the liquid. If enough has not entered in this way, the operation must be repeated. As soon as there is a sufficient quantity in the bulb the end of the tube is sealed off, any liquid contained in the tube being removed by warming. The bulb and its contents are now weighed, the difference in weights giving the amount of liquid

taken.   On proceeding to analysis, the bulb is laid in the boat, the tube being directed upwards, and its end is cut off, so that the vapour of the liquid can escape. The combustion is then proceeded with in the usual way.   The student should analyse glacial acetic acid in this way. Another method for the estimation of carbon and hydrogen in these substances will be described later.

Estimation of Carbon and Hydrogen in Nitrogenous Substances.—Nitrogenous substances, when burnt in a stream of oxygen in the way just described, usually give off some of their nitrogen as oxides.   These are absorbed by the potash, and the percentage of carbon consequently comes out too high.   In order to obviate this a copper
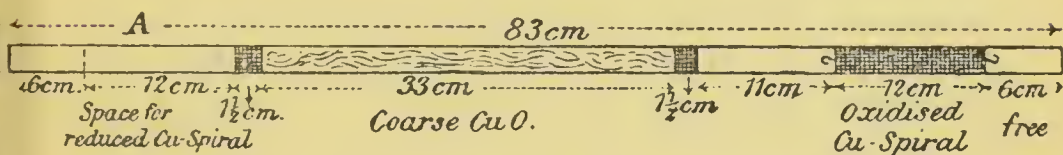
Fig. 18.

spiral must be placed in the tube at A (fig. 10), by which means the oxides are reduced.   The tube is, therefore, packed in the manner shown in fig. 18, space being left at A for the introduction of a reduced copper spiral before the combustion.   With the exception of this spiral the contents of the tube are roasted in a stream of oxygen, in the manner previously described; but before proceeding to analysis, *the oxygen must be displaced by air*.   The copper spiral is made in the same way as the oxidised copper spiral at the other end of the tube; in order that it may have a bright metallic surface, and at the same time contain no organic matter, it must be ignited and reduced. This may either be done by strongly heating in a current of

hydrogen, or more conveniently by the following method :— About 1 c.cm. of methyl alcohol is poured into a test-tube, itself 2 or 3 cm. longer than the spiral, the tube is then wrapped round with a duster, whilst the copper spiral, held in a pair of tongs, is heated to redness in a large blow-pipe flame. After a minute or two at this temperature the hot spiral is dropped into the test-tube ; the methyl alcohol is thereby volatilised, and its vapour reduces all copper oxide on the surface of the spiral, which should now have a very bright metallic appearance. The tube and its contents are then heated to 110° for at least an hour ; the tube is loosely corked, and when quite cool the cork is fixed firmly in place.

The student, having made the necessary preparations, should carry out the analysis of acetanilide and nitro-benzene. Weigh the calcium-chloride tube and potash bulbs, also the acetanilide into a porcelain boat. The tube having been roasted and cleared with air, as above described, the portion from A to B being at a dull red heat, the copper spiral is placed at A, tongs being used for the purpose. The calcium-chloride tube and potash bulbs are then attached, and the cock between the drying apparatus and tube being shut, the apparatus is tested as to its air-tightness by drawing air from the end of the potash bulbs with a piece of india-rubber connection tubing, as previously described. If every connection is thus found to be air-tight, the india-rubber stopper at the end of the tube next to the drying apparatus is taken out, the oxidised copper spiral removed, the boat placed in its position in the tube, and the oxidised copper spiral and india-rubber stopper replaced. The burners under the oxidised spiral are now lighted, but no oxygen or air is admitted from the drying apparatus, otherwise the reduced copper spiral would be rendered useless. As soon as the oxidised spiral is at low-

redness, the burners under the boat are turned on one by one, the substance being burnt as far as one is able by volatilisation into the layer of copper oxide. When this process has been carried as far as possible, it will be found that whilst some of the carbon has been carried into the bulbs as carbon dioxide, that a considerable quantity remains in the neighbourhood of the boat in an uncombined condition as charcoal ; the burners under the reduced spiral are therefore turned out, and a slow stream of oxygen is passed through from the drying apparatus until all the carbon is carried away as oxide, and free oxygen can be detected with a glowing splinter at the end of the potash bulbs. The oxygen is then replaced by a current of air and the combustion finished off in the usual manner. In performing the analysis of nitrobenzene, the liquid should be weighed into a bulb (see that the boat and bulb will easily pass into the tube), and the operation conducted as described on page 34.

Estimation of Carbon and Hydrogen in Substances which contain a Halogen.—The halogen compounds of copper are somewhat volatile, and also liable to give off some chlorine on heating in a current of oxygen, it is therefore necessary to place a substance in the tube which will retain the halogen in combination. This result is most easily attained by fitting up the tube in the same way as for a nitrogenous substance, replacing the reduced copper spiral, however, by a silver spiral. A tube fitted with such a silver spiral may be roasted in the ordinary way in a current of oxygen without any special precautions being taken, the silver spiral being in its position in the tube ; moreover, the combustion can be conducted throughout in a current of oxygen, clearing only with air at the end. The student should estimate carbon and hydrogen in paradibrombenzene.

Carbon and Hydrogen in Substances containing Sulphur.
—In the case of compounds containing sulphur, copper
oxide is not to be used, as it allows sulphur dioxide to pass
on, so that it is finally absorbed by the potash bulbs, with
the result that the carbon comes out too high. To avoid
this the tube from A to B (fig. 10), instead of copper oxide,
is charged with lead chromate, which, whilst oxidising carbon
compounds to carbon dioxide, retains sulphur dioxide in
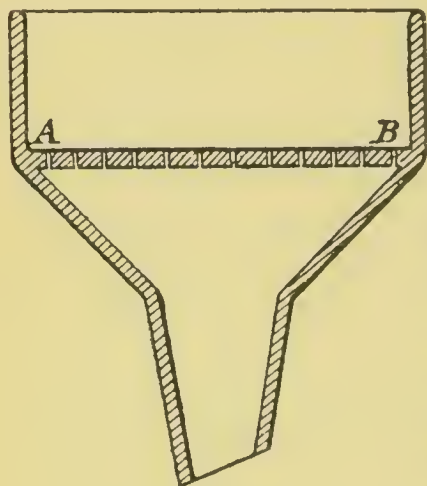the form of lead sulphate. To make the lead chromate,
weigh out 500 grams of lead
acetate and dissolve this in
two litres of warm water; add
to the solution so obtained a
solution of potassium dichro-
mate as long as a precipitate
forms (the solution may be
made from 400 grams of
potassium dichromate). After
vigorous stirring allow to settle,
wash with warm water by de-
cantation about 6 or 8 times.
Finally, collect the precipitate
on the filter through which the
washings, if they held any lead chromate in suspen-
sion, have been passed. Now wash thoroughly with
hot water on the filter until nothing but water can be
detected in the filtrate. The separation of a large quantity
of precipitate such as one has to deal with in this case can
be most quickly effected by a large Buchner's funnel.
Such a funnel has the form represented in figs. 19 and 20,
the former being a section of the funnel, the latter the
funnel and filter bottle as adapted for a filtering operation.
The funnel is fitted by a rubber stopper into the neck of a

FIG. 19.

filtering bottle, and on the perforated base, $A\ B$, two thicknesses of filter paper are laid. These are moistened, and on exhausting air through the tubulus C (fig. 20) the paper is drawn down, so that any liquid poured into the funnel must of necessity pass through the paper. We have in fact the funnel and filter plate of fig. 2 all made in one piece of porcelain. On ac-count, however, of the large area of the base, $A\ B$, a considerable quantity of material can be quickly filtered, the saving of time in substances difficult to filter being especially great.

The lead chromate, after being filtered and thoroughly washed in this way, is next dried and then carefully fused in a Hessian crucible; when quite melted it is poured out into a basin containing water. By this means it is obtained in a form which is easily broken up, it is therefore dried and reduced to granular fragments of a size suitable for the tube.

Fig. 20.

The tube being packed with lead chromate is next roasted in a stream of oxygen, just as a tube containing copper oxide would be, except that great care must be taken that the temperature does not get too high, otherwise the lead chromate will fuse and attach itself to the glass.
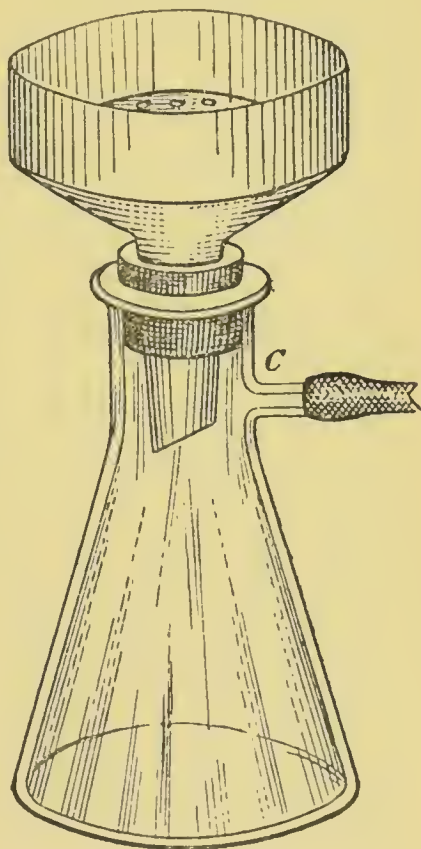
In carrying out a combustion this point must again be observed; moreover, the 10 or 15 cm. of lead chromate at the end, A (fig. 10), of the tube should be very moderately heated, since lead sulphate is not absolutely stable on ignition. Estimate the carbon and hydrogen in benzene sulphonyl chloride, $C_6H_5SO_2Cl$ (a liquid). Note that although a halogen is also present, no silver spiral is necessary, since the lead chromate will also keep back halogens.

A point worthy of notice is, that although a tube charged with copper oxide can be used repeatedly, since copper reduced by the organic substance is always re-oxidised by the oxygen stream, this is not so in the case of lead chromate; once reduced, it is not reoxidised, the tube can therefore only be used for a limited number of combustions.

The student should also make one or two estimations of carbon and hydrogen in the salts of metals which form carbonates stable towards heat. In this case it is obvious that the whole of the carbon will not be weighed as carbon dioxide in the potash bulbs; unless means are taken to expel the carbon dioxide from the more or less stable carbonate which is formed. The end may be obtained by mixing the substance in the boat with dry pure finely-powdered potassium dichromate. Carry out in this way the estimation of carbon and hydrogen in sodium benzoate and calcium oxalate. Although the latter salt contains no hydrogen, use nevertheless a calcium-chloride tube as in an ordinary estimation, weighing both before and after the combustion.

In estimating carbon and hydrogen in compounds containing mercury, a reduced copper spiral is placed in the front end of the tube, as in the combustion of a nitrogenous

substance, but heat very moderately. Mercury will thus be volatilised on to the copper and amalgamate with it; too high a temperature will, however, again break up the copper amalgam.

Combustion in Closed Tubes.—In the original combustion process devised by Liebig, the substance was intimately mixed with copper oxide and burnt at the expense of the oxygen of this compound. A slight modification of Liebig's original method may be advantageously employed in the combustion of liquids, and also liquids or solids containing nitrogen.

Estimation of Carbon and Hydrogen in Nitrobenzene.—Draw a piece of combustion tubing into the shape shown
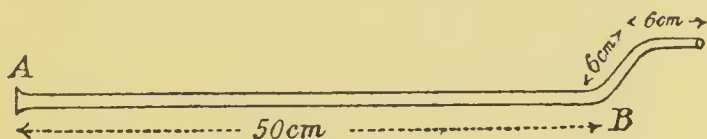

FIG. 21.

in fig. 21. This can be done if several centimetres of the tubing are softened in a large blowpipe flame, the bayonet portion of the tube being then cut off to the right length and its edges fused. The edges at the other end are also fused, so as not to cut the india-rubber stopper, which must be introduced here to carry the calcium-chloride tube. After the ends are cold, clean the tube out with finely-powdered potassium dichromate and strong sulphuric acid, then with distilled water, and stand the tube vertically, to drain as far as possible. To thoroughly dry the tube before combustion, a rubber stopper, through which the end of a straight calcium-chloride tube passes, is inserted at *A*; the tube is then clamped in a horizontal position; *B* is connected with a filter-pump; and, whilst a current

of air is aspirated through the tube, the latter is gently
warmed by drawing a Bunsen flame backwards and for-
wards along its length. When the tube is thoroughly
dry, the tube to the filter-pump is disconnected, and the
end, *B*, closed by a stopper similar to those used for
closing potash bulbs and calcium-chloride tubes. When
cold, the further end of the calcium-chloride tube may also
be protected with a similar stopper. The tube is now
ready for use.

Meanwhile, copper oxide may be ignited ready for use.
Be provided with 400 grams of coarse and 100 grams

FIG. 22.

of fine copper oxide. Care should always be
taken in the selection of fine copper oxide, since
much of it is made from copper nitrate by igni-
tion, and hence still contains appreciable quan-
tities of nitrogen. A good product can be
obtained by roasting copper filings in the muffle
with access of air, and afterwards grinding and
sifting the product. The copper oxide, whether
coarse or fine, required for a combustion must
be heated at least to dull redness for an hour
or more ; a considerably higher temperature can
be employed without any harm. The heating can
be conducted in large porcelain or copper cruci-
bles over a triple Bunsen flame or in a small muffle furnace.
The copper oxide, whilst still warm, is turned into flasks,
which are closed with corks provided with calcium-chloride
tubes (see fig. 22). Two flasks are required, one for the
coarse, the other for the fine, oxide.

Besides the copper oxide, four short oxidised copper
spirals are needed, made by rolling up strips of copper
gauze about 10 cm. in length by $1\frac{1}{2}$ cm. in width. These
fit the tube fairly easily, so that they may be put into and

removed from the tube with ease. A reduced copper spiral 10 or 12 cm. in length, prepared in the way previously described, is also needed.

The filling of the tube is carried out in the following manner. A fairly heavy retort stand is brought to the edge of the working bench, and the tube clamped in a vertical position, as shown in fig. 23. One of the short oxidised copper spirals is held in the tongs over a Bunsen
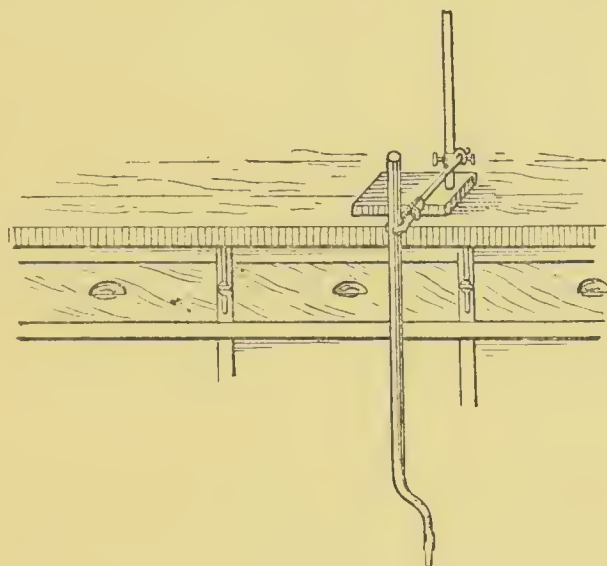
Fig. 23.

flame, so as to ignite it thoroughly; it is removed from the flame, allowed to nearly cool, and still warm dropped into the combustion-tube. This forms a plug at the narrow end, on to which coarse copper oxide is turned for a depth of 10 cm. with the aid of a copper funnel (or glass funnel with sufficiently wide neck). Another oxidised short spiral is now similarly ignited, and brought into the tube after it has cooled somewhat; this is succeeded by about 3 cm. of the fine oxide. A piece of glass rod, about 5 mm. diameter by 1 cm. in length, is now

dropped in ; the sealed bulb, containing ·15 to ·2 gram nitrobenzene, is allowed to fall on this, whereby it is broken. Fine copper oxide is again introduced, so that the total length of the fine oxide is about 6 cm. This is succeeded by another oxidised copper plug ; then come 20 cm. of coarse copper oxide, another oxidised plug, and finally the reduced spiral. The tube is now laid hori- zontally on the bench and gently tapped, so as to make an air passage along the top of the fine copper oxide ; it can then be placed in the furnace, and the calcium chloride tube and potash bulbs attached. Without removing the stopper at the end of the bayonet tube the whole apparatus must be tested to see if it is air-tight. Before proceeding
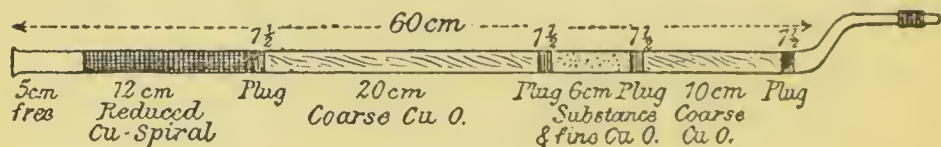

Fig. 24.

to the combustion, disconnect the stopper on the bayonet end ; replace it with a piece of sound connection tubing provided with a pinch-cock close to the bayonet. This connection-tube leads to the drying apparatus, so that a current of dry air may be passed through the tube at the end of the combustion.

The burners are now lighted under the reduced spiral and first 15 cm. of the coarse copper oxide, counting from the spiral, also under the 5 cm. of copper oxide next to the bayonet, taking care, however, that the connection tubing is in no way damaged by the flames. About twenty minutes later these two layers of the copper oxide should have attained a red heat, and now the flames may be turned up one by one, counting from the bayonet end of

the tube. This must be done gradually, so that the whole of the nitrobenzene is not burnt at once, but only gradually; the process will last about forty minutes. When all the nitrobenzene is burnt, the potash solution will be seen to suck back in the potash bulbs rising considerably in the bulb next to the calcium-chloride tube; this is due to the absorption of the carbon dioxide by the potash. By turning on the screw pinch-cock a slow stream of air is passed from the air gasholder through the tube by way of the drying apparatus; with about two bubbles per second (noted in the potash bulbs), about fifteen minutes will be necessary to clear the tube of all carbon dioxide. The flames in the combustion furnace are extinguished as soon as the calcium chloride tube and potash bulbs have been disconnected; the latter are stoppered and put in the balance case to cool.

As soon as the tube is cold, the contents should be turned out on to a piece of clean glazed paper, care being taken to keep the coarse and fine copper oxides separate as far as possible. This is fairly easy on account of the oxidised copper plugs employed; a final separation may be effected with a fine sieve. The two sorts of copper oxide should now be roasted and returned to their respective flasks; the copper spiral should be reduced and baked, in order to be quite ready for the next analysis. The small oxidised plugs may be kept in a well-corked test-tube.

Carbon and hydrogen should also be estimated by this method in a solid substance; take acetanilide for the purpose. The substance is finely powdered, dried on a watch-glass in the desiccator, and placed in a clean dry weighing-tube. In carrying out the analysis exactly the same process can be followed as with the liquid nitro-benzene, except in the way the substance is mixed with

the copper oxide. This is effected by placing some of the dry oxide in a clean dry glazed porcelain mortar; the weighing-tube and its contents are weighed, ·15 to ·2 gram of the substance is tilted out of the tube on to the surface of the copper oxide in the mortar, some more copper oxide is placed on the substance, which is then intimately mixed with the copper oxide by means of a glazed pestle, and copper oxide and substance are then introduced into the tube by aid of a funnel. The mortar is rinsed two or three times with fine copper oxide, the rinsings being introduced into the tube. The filling of the tube is then proceeded with in the usual manner, and the analysis carried out as previously described.

Estimate the carbon and hydrogen in a redistilled specimen of chloroform by this process, replacing the copper spiral by an ignited silver spiral. Since chloroform contains only about 10 per cent. of carbon, use at least ·4 to ·5 gram of the liquid, and take great care in heating the tube, since the chloroform is very volatile.

Estimation of Nitrogen in Organic Compounds.—The estimation of nitrogen in organic compounds is effected by burning the substance with copper oxide; the water formed is condensed, and the carbon dioxide absorbed by passing through a strong solution of caustic potash, whilst the nitrogen is collected and its volume measured. In order to do this it is necessary to displace all the air in the apparatus by carbon dioxide, otherwise the air in the tube would be collected and measured with the nitrogen. The apparatus required for an analysis of this kind is—

1. A combustion-tube 60 cm. long, one end fused and rounded off, the edges of the other open end being fused and slightly opened to receive an india-rubber stopper.

2. Four hundred grams of coarse copper oxide and

100 grams of fine copper oxide, contained in flasks fitted with calcium chloride tubes, as previously described.

3. A smooth pestle and mortar.

4. A copper funnel.

5. Pure sodium bicarbonate. Test this carefully for ammonia ; if it contains any it is useless.

6. A reduced copper spiral.

7. Four oxidised copper plugs.

8. A Schiff's nitrometer.

The filling of the tube, which must be cleaned with bichromate and sulphuric acid, well washed with distilled water and dried, is carried out in a manner very similar to
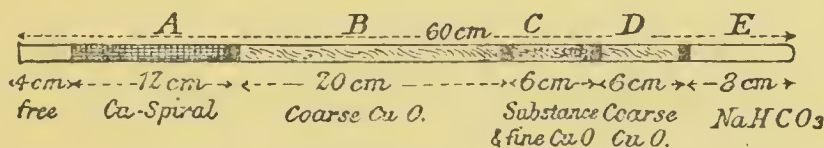

FIG. 25.

that adopted in the case of carbon and hydrogen estimations, the tube being clamped vertically at the edge of the bench. The first 8 cm. are filled in with sodium bicarbonate ; then comes an ignited plug of oxidised copper gauze (cold), next 6 cm. of coarse copper oxide, another plug, the substance mixed with fine copper oxide and rinsings from the mortar, the mixing being carried out as previously described ; another copper plug, 20 cm. of coarse copper oxide, another plug, and finally the reduced copper spiral. This will leave 4 cm. at the open end of the tube free. The tube is then laid horizontally on the bench, and gently tapped to make an air-passage at the top of the fine copper oxide and sodium bicarbonate. It is then laid in the trough of the combustion furnace, which is tilted so that the end at which the sodium bicarbonate is situated is

20 to 25 mm. higher than the other end. This obviates
cracking the tube during the process, owing to the
collection of water near the copper spiral. The tube is
fitted with an india-rubber stopper carrying a glass tube,
slightly bent, and connected with the lower, upwardly bent
side tube of the Schiff's nitrometer, which is filled nearly
as far as the upper of the side tubes with mercury. This
upper side tube is connected by india-rubber tubing with a
bulb held in a clamp or a ring attached to a retort stand.
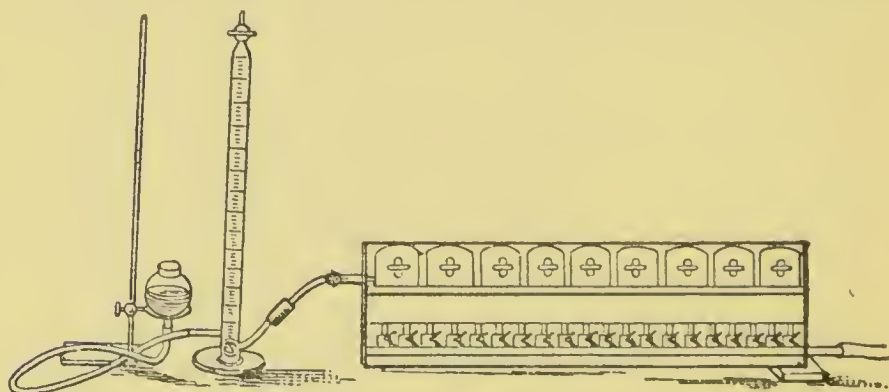Into this bulb, the capacity of which is somewhat greater

Fig. 26.

than that of the graduated tube, enough 50 per cent.
potash solution is poured to rather more than fill the
graduated tube when the bulb is raised. Everything
being arranged in the way shown in fig. 26, one may
begin the heating of the tube. One burner is lit at the
extreme end, E (fig. 25), the bicarbonate as it is heated
yielding carbon dioxide with great ease. The height of this
one flame must be carefully attended to, lest the evolution
of carbon dioxide be too rapid. During this process the
bulb should be in its lowest position, as shown in the
figure, and the cock of the nitrometer be wide open.
There is no necessity to spoil the potash more quickly

than need be helped. After a brisk current has been passing for about ten minutes, see whether the tube is entirely cleared of air. This is done by raising the bulb, so that the whole of the graduated tube is filled with the potash solution, then shutting the cock and lowering the bulb to its former position. If the bubbles of gas are entirely absorbed as they rise through the potash, it is evident that the whole of the air has been expelled from the tube. On the other hand, if air is still present, the potash solution should be returned to the bulb by opening the cock, and the heating of the bicarbonate proceeded with. The idea of combustion must not be entertained until nothing more than an immeasurably small quantity of minute foam succeeds in passing the caustic potash solution. The burners under the copper spiral, A (fig. 25), may, however, be lighted when the current of carbon dioxide has been passing for only five minutes without any danger of the copper spiral becoming appreciably oxidised. It is as well to have the copper spiral at dull redness before the air is finally cleared from the nitrometer prior to the actual combustion of the substance. This is on account of the possible occlusion of gases by the copper, which, being expelled on heating, would increase the volume of the nitrogen. The spiral being red hot, all air expelled from the tube, the cock of the nitrometer closed, the graduated tube entirely filled with the potash solution, and the bulb in its lowest position, the burners under the first 15 cm. of copper oxide after the copper spiral can be lighted, whilst the burner under the bicarbonate is turned very low. As soon as this layer is at dull redness one or two burners under the layer, D, of copper oxide should be lighted; this is to prevent any of the substance volatilising backwards along the tube. Take care, however, that the heat-

E

ing does not extend to the bicarbonate. There is no need
to have a continuous stream of carbon dioxide during the
process. The bicarbonate must, however, be saved so as
to yield enough carbon dioxide to entirely clear the tube
at the end of the combustion. The middle portion of the
copper oxide at D being fairly hot, the intermediate
burners between this point and the coarse copper oxide at
B may be lighted one by one. This stage will occupy
thirty minutes or more, for during the period the sub-
stance will be entirely burnt, partially at the expense of
the oxygen of the fine copper oxide with which it is mixed,
in part, however, by the oxygen of the coarse copper oxide.
In this way all the carbon of the compound is converted
into carbon dioxide and the hydrogen into water, whilst
the nitrogen is partially evolved in the free state, partially,
however, as oxides. The latter are, however, reduced to
free nitrogen by the red-hot copper spiral, so that all the
nitrogen, and nothing but nitrogen, collects in the nitro-
meter. When the combustion is complete, as seen by the
volume of gas in the nitrometer undergoing no appreciable
alteration, the tube is once more cleared by a stream of
carbon dioxide, obtained by lighting up one or two of the
burners under the bicarbonate. As soon as nothing but a
minute quantity of foam collects on the surface of the
potash solution the volume of gas is noted, and if this does
not appreciably alter during a further five minutes, the com-
bustion may be taken as complete. The combustion tube
and the nitrometer are now disconnected, the connection
tubing being left attached to the side tube of the nitrometer.
The tubing should be tightly closed by means of a pinch-
cock. The nitrometer is removed from the neighbourhood
of the furnace and allowed to stand for forty-five minutes.
In reading the volume of nitrogen raise the bulb so that the

level of the potash solution is the same inside the graduated tube and in the bulb, and take care that when making the reading the eye is also on the same level, so as to avoid error due to parallax. The lowest part of the meniscus is taken for the reading. Note the temperature of the potash solution in the nitrometer. This is a safer way to determine the temperature of the nitrogen than reading a thermometer hung on the outside of the nitrometer. The height of the barometer is also noted at the same time.

If v be the observed volume of nitrogen, its volume, corrected to $0°$ and 760 mm. pressure, will be—

$$v \, \frac{273 \times (B - f)}{(273 + t)\,760}$$

where B is the height of the barometer in millimetres of mercury, t the temperature in Centigrade degrees, and f the vapour pressure of a 50 per cent. potash solution at $t°$. This quantity, f, is somewhat uncertain; at any ordinary temperature it is roughly one-third of the vapour tension of water at the same temperature. Since the weight of 1 c.cm. of nitrogen at $0°$ and 760 mm. pressure is $\cdot001256$ gram, we shall have the percentage of nitrogen in the substance equal to—

$$\frac{v \times 273 \times (B - f) \times \cdot 1256}{(273 + t) \times 760 \times w}$$

where w is the weight of the substance taken.

Stress has been laid on the necessity that the sodium bicarbonate is free from ammonia; it is very likely to contain the latter, since it is frequently produced by the ammonia-soda process. Various substitutes may be used instead of bicarbonate, magnesite in the size of small peas being frequently employed. The layer of magnesite

should occupy about 15 cm. of the tube. Again, when a mixture of normal sodium carbonate and potassium dichromate is heated, carbon dioxide is evolved according to the equation—

$$Na_2CO_3 + K_2Cr_2O_7 = Na_2CrO_4 + K_2CrO_4 + CO_2.$$
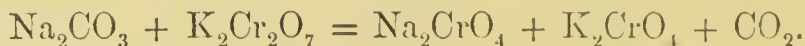
A finely-powdered mixture, in the proportion of one part by weight of the former to three parts by weight of the latter, may therefore be used. It will be found, however, that both magnesite and the bichromate mixture must be more strongly heated to give off carbon dioxide than sodium bicarbonate.

Another modification consists in the generation of carbon dioxide outside the tube, which must therefore be open at both ends, either bayonet-shaped or arranged in a very similar way to an ordinary open combustion tube. The carbon dioxide is generated from a Kipp's apparatus; the marble employed should be previously boiled for some hours in water, in order to expel any air occluded in its pores. Even under these circumstances the clearance of air from the tube is not always very accurately carried out.

A method which furnishes very accurate results, but which is not frequently used, on account of the time occupied, consists in exhausting the tube completely whilst in the furnace by means of a Sprengel mercury pump. The combustion is then proceeded with, the copper spiral being first heated, and the heating being gradually extended along the tube to the other end, all gas evolved being pumped out by means of the mercury pump. The carbon dioxide and nitrogen formed are collected over mercury; after absorption of the former by a small quantity of strong potash solution, the graduated

tube is transferred to a cylinder of water, in which it is left for some time to acquire the same temperature. In reading the volume of gas, the graduated tube is raised in the cylinder until the water stands at the same level inside and outside the tube; in correcting for temperature and pressure, the whole vapour pressure of water at the particular temperature must be taken into account. If the total volume of carbon dioxide and nitrogen is measured accurately, and the carbon dioxide then absorbed by potash, the nitrogen being afterwards read in the usual way, we are able to estimate both carbon and nitrogen at one and the same time.

In the collection of nitrogen, when making an analysis by the method described in full above, a very important modification may be made by which means uncertainty as to the vapour pressure of the potash solution may be wholly avoided. The Schiff's nitrometer need not be graduated, but a graduated tube must be employed. The tube of the nitrometer is connected with a bent tube
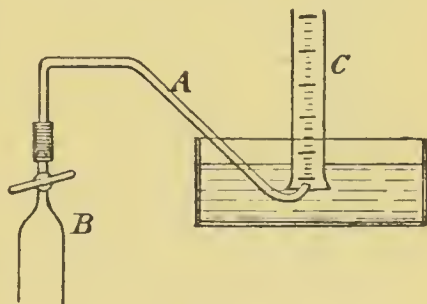

FIG. 27.

passing into a pneumatic trough, as shown in fig. 27. In carrying out the combustion the tube is cleared of air in the previously described manner by means of a stream of carbon dioxide; when it is wished to arrange the tube for the collection of nitrogen, the bulb of the nitrometer is held at such a height that the whole of the air is displaced from the nitrometer, and also from the leading tube, A, which is dipping under the surface of the water in the small pneumatic trough. As soon as the last

bubble of air is expelled from the end of the leading tube
in this manner, combustion can be proceeded with, and
the nitrogen collected at the top of the tube, B. At the
end of the process the nitrogen, instead of being read off
directly in the tube B, is transferred to the measuring
tube, C, by opening the cock at the top of B after the
bulb has been raised to a level slightly higher than that of
the leading tube, A. All the nitrogen being transferred,
the cock is shut off, so as to avoid waste or weakening of
the potash solution by its escape into the trough, or by
water running from the trough into the tube, B. The
thumb is then placed firmly under the mouth of the

Fig. 28.

tube, C, which is transferred with its contents
to a glass cylinder filled with water, represented
in fig. 28. After standing in this for twenty
minutes to half an hour, the tube is raised, so
that the water stands at the same level inside
and outside the tube, and the volume is read
off, whilst the temperature of the water in
the cylinder is noted. The barometer is of
course read at the same time. The calculation
of the result from the volume of nitrogen
obtained is precisely similar to that previously explained,
except that the full vapour pressure of water must be
subtracted from the barometric pressure.

A method which was formerly much employed, and is
still in use in many commercial laboratories, depends on
the evolution of nitrogen in the form of ammonia on
heating with soda lime. The general arrangement is
represented in fig. 29, the ammonia being collected in a
known volume of standard sulphuric acid contained in
a suitable bulb apparatus, such as that represented, or of
other patterns. The bicarbonate at the closed end of the

tube is used at the end of the process to supply a current of carbon dioxide to clear all the ammonia into the sulphuric acid. The amount of ammonia evolved is determined by finding how much of the sulphuric acid has been neutralised. To do this the contents of the bulb are transferred to a beaker, the bulbs rinsed two or three times with distilled water, and the rinsings added; the uncombined sulphuric acid is then determined by titration with standard soda solution, a drop of methyl orange having been added as an indicator.

The ammonia may also be gravimetrically estimated by using hydrochloric acid in the bulbs in place of
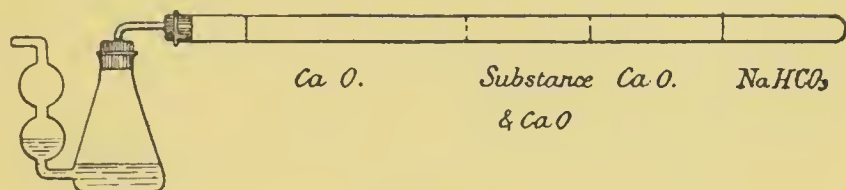

Fig. 29.

sulphuric acid, and afterwards precipitating the ammonia as ammonium chlorplatinate, which may either be dried and weighed as such, or ignited and the residual platinum weighed.

The method has been but briefly sketched, as it is now used but slightly for scientific work, since good results are only obtained with compounds which can be considered to be of the ammonia type. Practically no ammonia is evolved on heating nitro-compounds or organic nitrites or nitrates with lime.

The results obtained by combustion with copper oxide are, however, generally reliable whatever type of compound be analysed.[1]

[1] Compare, however, Dunstan, *Proc. Chem. Soc.*, 1896. No. 161, p. 48.

Estimation of the Halogens.—The halogens are now usually estimated in the manner devised by Carius, which depends on the total destruction of the organic matter by heating to a high temperature (200°) with fuming nitric acid in presence of silver nitrate. The halogen then combines with the silver, and is estimated in the usual way. The following apparatus and material are required for the carrying out of such an analysis :—

1. An oven provided with a thermometer and heated by gas.

2. Stout walled glass tubing, outside diameter about 20 mm., the glass should be 2 or 3 mm. thick. Good soda glass is preferable ; it is easy to work in the blow-pipe flame. Lead glass must be carefully avoided. Hard glass—combustion tubing—may be used, but it is very difficult to work.

3. A small specimen tube about 6 to 8 cm. long and about one-tenth this diameter.

4. A thistle funnel.

5. Pure crystallised silver nitrate and fuming nitric acid of sp. gr. 1·5. This must be tested for halogens by diluting largely with distilled water and adding a few drops of silver nitrate solution. If the nitric acid shows the slightest trace of the presence of halogens, it must be poured into a retort containing a small quantity of powdered silver nitrate, shaken from time to time, and after some hours carefully distilled off, care being taken that no frothing occurs during the distillation.

6. The usual apparatus used in gravimetric analysis, such as beakers, funnels, clock glasses, glazed paper, porcelain crucible, desiccator, &c.

The tube in which the heating with nitric acid is to be carried out must be sealed off with an even rounded

end at one extremity, its length being from 40 to 50 cm. In making the seal care must be taken that the rounded end is as thick as the walls of the tubing. This is best effected by turning the tube slowly round in the blowpipe flame until the glass at this end has acquired a considerable thickness, and then removing the tube from the flame and blowing very gently into it, the tube being rotated slowly during the blowing operation. Before proceeding further the tube should have the shape shown in fig. 30. When the tube has the desired shape the sealed end is annealed by holding it in a luminous flame until it is covered with soot, then removed and allowed to cool very slowly. When cold it is cleaned by means of
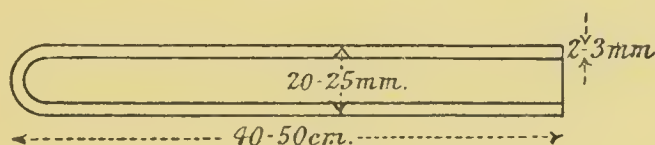

FIG. 30.

finely-powdered potassium dichromate and strong sulphuric acid, rinsed several times with distilled water, and clamped in an inverted position to drain. The tube is finally dried by gently heating it and introducing a current of air.

The specimen tube which has been cleaned, dried, and left in the desiccator is now accurately weighed. About ·2 gram of the substance is now introduced into it, the open end is wiped clean, and the tube and its contents again weighed. In this way the quantity of substance taken for analysis is determined. The tube is then returned to the desiccator.

The dried pressure tube is now clamped vertically with its open end upwards, and from ·5 to 1 gram of silver nitrate and about 4 c.cm. of the pure fuming nitric acid

introduced by a thistle funnel. The tube of the thistle
funnel should reach nearly to the bottom—within, say,
5 or 10 cm.—of the pressure tube. When afterwards
withdrawing it take care that the lower end does not wet
the sides of the pressure tube. The latter is now removed
from the clamps, held in an inclined position, and the
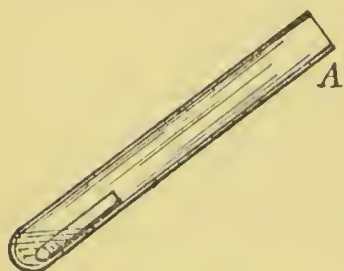specimen tube with its contents are carefully slipped
inside. The nitric acid must on
no account be allowed to come in
contact with the substance until
the end, A, is also closed, conse-
quently during the sealing opera-
tion do not incline the tube to a
greater extent than is shown in
the sketch. The end, A, is now
gradually heated by holding it in the large luminous
flame of a blowpipe, turning the tube round continually;
only begin to work the bellows slightly when the outside of
the tube has become well blackened with soot. By gradu-
ally increasing the blast the tube may be safely raised to a
high temperature. When the open end, A, is soft, a heated
glass rod is fused on to one side, pressed across to the other
side, and the union between rod and tube made good by
further heating. The blowpipe flame is now turned down
until only 8 or 10 cm. long; in this flame the tube is strongly
heated at the point B, until the glass has thickened very
considerably, as shown in fig. 33. During this process the
tube and attached glass rod must be continually turned, so
that the thickening may take place equally all round.
When the glass has thickened considerably the tube is
removed from the flame and slowly drawn out into a
capillary tube, which is sealed off, the tube now having
the appearance shown in fig. 34. This end of the tube is

FIG. 31.

now thickly coated with soot in a luminous flame, the tube then removed from the flame, clamped in a vertical position, and allowed to cool. When the tube is cold it may be turned
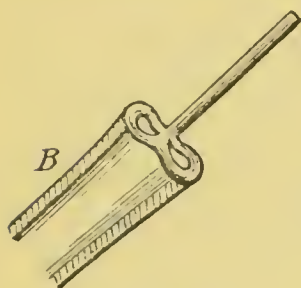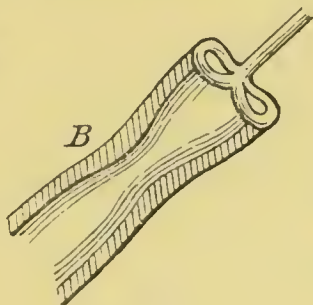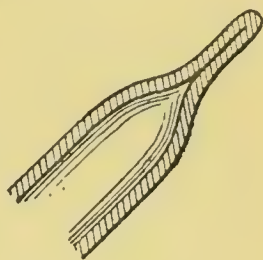

FIG. 32.   FIG. 33.   FIG. 34.

into the horizontal position, so that the nitric acid comes in contact with the substance. Before placing the tube in one of the iron cases of the oven it should be wrapped round with one or two layers of paper. This serves the
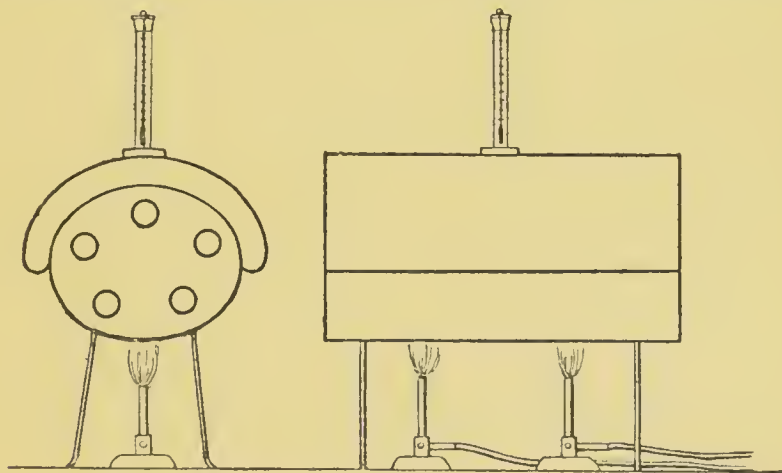

FIG. 35.

double purpose of keeping the tube from being scratched or from unequal heating in contact with the metal. A generally useful form of oven for the heating process is shown in end and side elevation in fig. 35. The end

elevation shows the iron tubes in which the sealed pres-
sure tubes are placed.   In order to avoid damage in case
of explosions the ends of the furnace should be protected
with stout iron plates.

The tubes for halogen estimations being placed in the
oven, heating may be begun.   It is preferable to use two
or more burners for this purpose instead of one large
flame, so as to avoid overheating in any one part.   The
heating must be gradual, about two hours being occupied
in attaining 200°.   The oven should now be kept at 200°
for two to three hours, which is usually a sufficient time to
effect the complete decomposition of the substances, al-
though with some stable aromatic compounds, such as the
halogen substituted nitrobenzenes, at least six hours'
heating is necessary, the temperature being slowly raised
to 250°.   At the end of the heating the tube is first
allowed to cool inside the oven before it is withdrawn,
and must then be carefully wrapped round with a cloth,
as there is sure to be a very high pressure inside it.
Tubes which have been heated must on no account be
left, since they are liable to explode, and very dangerous
explosions may occur.

In opening the tube, the capillary portion is first
gently warmed, in order to drive any liquid it may con-
tain into the broader portion of the tube; the extreme end
of the capillary is now softened, when it immediately
blows out and a large volume of gases escapes.   The end
of the tube is now cut off by filing it all round rather
deeply, and applying a hot piece of glass to the file mark.

The contents of the tube are now turned out into a
porcelain dish, not into a beaker, since in this case there
is a considerable possibility of breaking the latter with
the specimen tube, and so losing the analysis.   The tube

is now rinsed out several times with distilled water into
the dish ; any silver halogen compound which obstinately
adheres to the sides of the tube may be removed by means
of a scrubber made of a piece of glass rod tipped at the
end with connection tubing. The whole of the contents
of the pressure tube being transferred to the dish, the
specimen tube is pushed to the edge by means of a piece
of glass rod, so that a portion comes above the surface of
the liquid. This projecting portion is well washed on the
outside with distilled water, and removed by the thumb
and forefinger of the left hand from the liquid ; the rest
of the outside can then be washed, and the interior of the
tube thoroughly rinsed out into the dish. We now have
in the dish dilute nitric acid and silver nitrate solution,
together with the whole of the halogen compound of silver.
Before filtering off the latter, warm gently for ten or fifteen
minutes with continual stirring, then collect in the usual way
on a filter, the weight of the ash of which is known. After
washing repeatedly with warm water, to which a drop of
nitric acid has been added, and testing a few drops of the
washings to see that all soluble silver compounds have
been entirely removed, the filter and its contents are dried
in a water-bath at 100°. When thoroughly dry, a piece of
glazed paper is placed on the bench, and on this are put
the filter with the silver chloride, and a porcelain crucible
which has previously been ignited, desiccated, and weighed.
The silver halogen compound is detached as completely
as possible from the filter paper, and transferred to the
crucible ; the filter paper itself is rolled up, put on the lid
of the crucible, and burnt on the latter to ash. When
cold the ash is moistened with a few drops of nitric acid
to effect the solution of the metallic silver which has been
reduced by the burning filter paper, then one or two

drops of the acid, corresponding to the halogen deter-
mined, are added, and the liquid on the lid is carefully
and slowly evaporated, care being taken that no loss
occurs through spirting. The crucible is now placed on a
pipeclay triangle, the lid placed on it (upside down), and
the crucible and its contents heated until the halogen
compound of silver shows slight signs of fusion at its
edges.   Prolonged ignition is to be avoided, since the
halogen compounds of silver are decidedly volatile when
strongly heated. The crucible and lid are transferred to
the desiccator and weighed when cold. By subtracting
from this weight the weight of the empty crucible and lid
and of the filter ash, the weight of silver halogen com-
pound is given; the calculation of the percentage of
halogen in the compound can then be made in the
usual way.

The halogen in liquids of high boiling point can be
determined in a precisely similar manner, since there is no
danger of evaporation during the weighing and sealing
operations. A method for estimating the halogen in easily
volatile liquids will be subsequently described. Meanwhile,
halogen estimations in parachloraniline, metabrombenzoic
acid, and iodobenzene (liquid) should be made.

A modification of this method of estimating halogen
consists in taking a known weight of silver nitrate,
according to the method previously described, and after
filtering off the halogen silver compound, estimating the
silver remaining in excess which is present in the filtrate,
by means of a standard solution of ammonium thiocyanate.
The results obtained are not as accurate as those obtained by
a good gravimetric analysis, still they furnish a useful check
on these, and, moreover, are not affected by an accident
which may easily occur, the admixture of small splinters of

glass when the tube containing the silver halogen com-
pound precipitate is opened.   To carry out an analysis
of this sort, weigh out accurately about 1 gram of silver
nitrate into the pressure tube, then introduce nitric acid
and substance, and heat in the way which has been de-
scribed.   After cooling and opening the end of the tube,
its contents are diluted with water, filtered, the tube and
precipitate carefully washed, and all washings added to
the filtrate.   To the collective filtrate a drop or two of the
indicator is added, made by dissolving a small crystal of
ferric alum in hot dilute nitric acid.   A solution of am-
monium thiocyanate is now run in from a burette, the
contents of the beaker being well stirred.   A white pre-
cipitate is formed, the end of the reaction being detected
by the red colour the solution assumes when all the silver
has been precipitated owing to the formation of ferric
thiocyanate.   The ammonium thiocyanate solution should
be of decinormal strength, *i.e.* 1 c.cm. precipitate, ·0108
gram of silver, or be equivalent to ·0170 gram of silver
nitrate.   If x be the weight of silver nitrate originally
taken, and y c.cm. of the thiocyanate solution are em-
ployed, the amount of silver nitrate which has been con-
verted into halogen compound will be—

$$x - ·0170\, y.$$

And if a be the atomic weight of the halogen present in the
substance, then the actual weight of the halogen present
in the quantity of substance taken will be—

$$a\left(\frac{x}{·0170} - y\right).$$

This method is, it will be noticed, useful for determining
the total amount of halogen in a substance where more
than one of the halogen elements is present.

It may also be applied to the analysis of volatile liquids in the following manner. When the weighed amount of silver nitrate and the necessary fuming nitric acid have been introduced into the tube, a small bulb is accurately weighed, some of the liquid is introduced into this, the end of the tube attached to the bulb is closed by heating, and the bulb and its contents are weighed. The bulb is then allowed to slide gently down inside the tube, taking care that it does not get broken. The tube is then sealed off at the end, and, when cold, the bulb is broken by shaking the tube, which can then be heated. In a case like this it is of course impossible to avoid the occurrence of splinters of glass with the silver halogen precipitate.

In the case of gravimetric estimations of chlorine, the silver chloride can readily be separated from splinters of glass by solution in warm dilute ammonia and reprecipitation with acid. This is, of course, not possible in the case of silver bromide and iodide ; the only way is to weigh glass and silver halogen compound together, then reduce the silver to the metallic condition, and remove it, by solution in warm dilute nitric acid, from the glass, which is washed well, collected, and weighed.

Estimation of Sulphur.—The estimation of sulphur closely resembles that of the halogens, the organic matter being destroyed by strong heating with fuming nitric acid, the cleansing and filling of the pressure-tube being carried out as for a halogen, except that the silver nitrate is replaced by barium nitrate. After heating and subsequent cooling, the contents of the tube are transferred to a porcelain dish, water added, the contents warmed, and the barium sulphate filtered off, well washed, dried at 100°, the barium sulphate detached as far as possible from the filter-paper and transferred to a crucible. The filter-

paper is then rolled up, wrapped round with platinum
wire, reduced to ash, and the latter added to the contents
of the crucible.   One drop of nitric acid and one of sulphuric
acid are now added (since barium sulphate is reduced to
sulphide on heating with carbonaceous matter), and the
crucible and its contents are strongly ignited and weighed.
If x be the weight of substance used for analysis and y the
weight of the barium sulphate obtained, the percentage of
sulphur in the substance will be

$$\frac{y \times 32 \times 100}{x \times 233}.$$

The student should carry out sulphur estimations in sulph-
anilic acid and thiourea.   In the latter case not more than
·15 gram of substance need be used, since its percentage
of sulphur is high.

Estimations of both sulphur and halogen may be made
with one and the same quantity of substance.   As in the
case of an ordinary halogen compound, the substance is
heated with fuming nitric acid and silver nitrate.   The
precipitate of silver halogen compound is filtered off and
estimated in the way previously described ; from the
filtrate the excess of silver is precipitated as chloride by
the addition of dilute hydrochloric acid, the silver chloride
removed by filtration, the filtrate then raised to boiling,
and the sulphuric acid precipitated by addition of barium
chloride solution.   The barium sulphate formed is then
treated in the usual fashion.   An estimation of this sort can
be carried out in benzene-sulphonyl chloride (a liquid).

Phosphorus is estimated in organic compounds by
heating with fuming nitric acid.   When the organic matter
is destroyed and the tube cool, its contents are diluted
largely with water, ammonia added until alkaline, and

F

then magnesia mixture. The beaker containing the mix-
ture is then allowed to stand in a warm place for twelve
hours, so as to ensure complete precipitation, the preci-
pitate of ammonium magnesium orthophosphate is then
filtered off, washed with dilute ammonia, and dried at
100°. The precipitate is then transferred from the paper
to a crucible, the filter-paper rolled up and burnt to ash,
the ash added to the rest of the substance in the crucible,
which, with its contents, is then ignited strongly. After
cooling, a drop or two of nitric acid is added to the con-
tents of the crucible, which is then ignited again for some
time at a red heat. This process is repeated until the
weight of the crucible and its contents is constant. If x
be the weight of substance taken, and y the weight of
magnesium pyrophosphate obtained by this method, the
percentage of phosphorus will be—

$$\frac{y \times 100 \times 31}{x \times 111}.$$

It will be noticed in the above-described process that no
preliminary separation of the phosphoric acid in the form of
phosphomolybdic acid is employed ; such procedure is only
necessary if the substance contains metals other than those of
the alkalies in addition to the phosphorus to be estimated.

The Estimation of Metals in the salts of organic acids
is usually carried out by some process of ignition, the
organic matter being thereby destroyed. In the case of
the salts of the alkalies and alkaline earths, the metal is
most conveniently weighed as sulphate ; the process will
be rendered evident by the following examples :—

Estimation of Calcium in Calcium Oxalate.—Pre-
cipitate a solution of calcium chloride (about ·5 gram)
with ammonium oxalate at a boiling temperature. Boil

vigorously for ten minutes, allow the precipitate to settle, pour the supernatant liquid through a plaited filter, wash the precipitate four or five times in the beaker with boiling water, stirring the precipitate each time with the fresh quantity of water, then allowing it to settle, and decanting the water through the filter, to which it is finally transferred and washed again several times with boiling water. Dry the precipitate thoroughly at 100°, and transfer it to a clean, dry weighing-tube. Ignite a
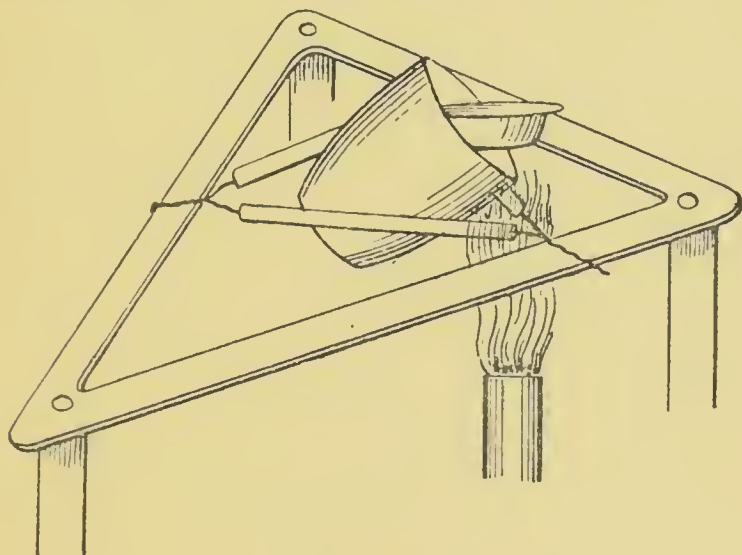

Fig. 36.

platinum crucible thoroughly, allow it to cool in a desiccator and weigh. Transfer about ·3 gram of the dry calcium oxalate to the crucible and weigh again. Now heat the crucible and its contents strongly for some time over a Bunsen flame. Allow it to cool, add two or three drops of strong sulphuric acid, and replace it on the pipe-clay triangle in an inclined position, with the lid nearly horizontal. Heat the upper end of the crucible first by placing the flame in the position shown in fig. 36. By

this means creeping of acid over the edge of the crucible is avoided. When all the excess of sulphuric acid has been volatilised, which may be recognised by the white fumes of sulphur trioxide ceasing, the crucible is more strongly heated all over, transferred to the desiccator, cooled, and weighed.

The case taken is very simple, since calcium oxalate decomposes on heating into calcium carbonate and carbon dioxide ; in most cases the first action of heat is to furnish a metallic carbonate and much free carbon. This must be burnt away before the treatment with sulphuric acid, otherwise the sulphate of the metal will be reduced to sulphide. In all cases where carbon separates it is advisable to repeat the ignition after adding a drop of sulphuric acid at least once, as by this means one is certain that the sulphuric acid will convert any sulphide which has been formed by reduction back into sulphate.

Many of the heavy metals may be estimated as oxides. It is usually as well to moisten the residue left after ignition with nitric acid, and then to ignite afresh, since reduction to the metallic condition will take place partially in many cases. Lead, however, may be conveniently estimated as sulphate, the residue, after the carbonaceous matter has been removed, being treated in the crucible with moderately dilute nitric acid, then gently warmed. a few drops of sulphuric acid added, and evaporated at a moderate temperature. The residue must then be gently ignited, cooled in the desiccator, and weighed. A platinum crucible must on no account be used for lead estimation.

Gold, platinum, and silver are left in the metallic condition when their organic compounds are ignited, since they do not oxidise in the air ; they are most readily

weighed in the metallic condition. Estimations of these and other easily reducible metallic salts must be carried out in porcelain crucibles.

In the case of mercury it is obvious that ignition methods cannot be used. Where only small quantities of mercury compounds are at the experimenter's disposal, it is best to destroy the organic matter by heating with fuming nitric acid in sealed tubes, after cooling to dilute the contents largely with water, and to precipitate the mercury with sulphuretted hydrogen. The mercury sulphide is collected on a tared filter, well washed with water, dried, and then washed with carbon disulphide to remove any admixed free sulphur. Finally, the filter-paper and precipitate are dried until the weight is constant.

CHAPTER III

DETERMINATION OF EQUIVALENT AND MOLECULAR WEIGHTS

THE determination of the molecular weight of a compound is obtained by finding its vapour density. In cases where the substance is not volatile, the lowering of the freezing-point or raising of the boiling-point of some suitable solvent, when a given quantity of the solvent is used to dissolve a known weight of the substance, is employed. In the case of substances of basic or acidic character, analysis of derivatives will usually furnish the equivalent weight; this is some simple submultiple of the true molecular weight. We shall, therefore, deal with the question of equivalent weight first of all.

Determination of the Equivalent Weight of Brucine ($C_{23}H_{26}N_2O_4$).—Dissolve about ·3 gram of brucine in the least possible amount of dilute hydrochloric acid; the latter should be added in small quantities at a time, and gently warmed to aid the solution of the base. Filter the solution if necessary, and add to the filtrate a solution of chlorplatinic acid. A yellow crystalline precipitate of the chlorplatinate will be thrown down; this is filtered off, washed repeatedly with small quantities of cold water, and dried in a desiccator over sulphuric acid. Now ignite a clean porcelain crucible, allow it to cool in a desiccator, and weigh accurately. Tilt into it about ·2 to ·3 gram of the chlorplatinate and weigh again; the difference of the two weighings will give the amount of salt taken. Now

heat the crucible and its contents over a Bunsen flame, at first gently, so as to avoid any loss of substance, then more strongly, the lid being somewhat tilted to burn away the carbon which separates on the initial heating.   When all the carbon seems to have been burnt, remove the crucible to the desiccator, allow to cool, and weigh.   The crucible must now be heated again for ten to fifteen minutes, cooled and weighed ; if the weight is constant, it may be taken that nothing but platinum remains in the crucible.   From the weight of platinum obtained, we can calculate the equivalent (in this case molecular) weight of the base, for we know that the chlorplatinates of bases have the general formula $B_2H_2PtCl_6$; where b represents an equivalent of the base.   Let b be the equivalent weight, x and y represent respectively the amount of salt taken and the weight of platinum formed,

then $$b = \frac{194\cdot3\ x}{2\ y} - \frac{409\cdot3}{2}$$

when $194\cdot3$ is the atomic weight of platinum and $409\cdot3$ the molecular weight of chlorplatinic acid, H_2PtCl_6.

Determination of the Equivalent Weight of Succinic Acid.—The equivalent weight of succinic acid may be determined by an estimation of the amount of silver in its silver salt ; this method can be applied in almost all cases, and furnishes accurate results.   Dissolve about ·2 gram of succinic acid in 50 c.cm. of distilled water, to which a few c.cm. of dilute ammonia have been added ; remove the excess of ammonia by boiling the solution until the smell of ammonia cannot be recognised.   Filter the solution if necessary, and precipitate by the addition of silver nitrate. The white flocculent precipitate of silver succinate is now to be filtered off, well washed with warm water and dried

in the desiccator over sulphuric acid. (Do not leave the desiccator in a light place, or the silver salt will become discoloured.) When quite dry, the silver succinate is transferred to a weighing tube; meanwhile a porcelain crucible and its lid are ignited, desiccated, and accurately weighed. Transfer about ·25 to ·3 gram of the silver salt to the crucible, which weigh again with its contents. The crucible must now be ignited, at first gently, afterwards more strongly, and brought to constant weight as described in the case of the brucine chlorplatinate. The silver will be left as a greyish finely-divided mass at the bottom of the crucible; let y be its weight, whilst x is the weight of the silver succinate taken for the estimation. If the equivalent weight of the acid be e, it is obvious that the equivalent weight of the silver salt is

$$108 + e - 1,$$

since 108 parts by weight of silver replace 1 part of hydrogen. Thus we have

$$\frac{x}{y} = \frac{e + 107}{108}.$$

when

$$e = \frac{108\,x}{y} - 107.$$

Since succinic acid is dibasic, two atoms of silver replace two atoms of hydrogen, and the equivalent weight must be doubled to give the molecular weight.

Determination of the Equivalent Weight of Oxalic Acid. In certain cases equivalent weights of acids cannot be determined by means of the silver salts, since some of these explode on heating. Thus, if silver oxalate be heated, the decomposition takes place suddenly and violently, and some of the silver is sure to be thrown out of the crucible.

In this case it is necessary to work with the salt of some other metal, *e.g.* barium.

Precipitate a solution of ammonium oxalate with barium chloride, carrying out the preparation in the manner described for calcium oxalate on page 66. The dry barium oxalate is converted into barium sulphate just as the calcium in calcium oxalate was obtained, and weighed as calcium sulphate. If x be the weight of barium oxalate taken, and y the weight of barium sulphate found, then we have the following equation, where e is the equivalent weight of oxalic acid :—

$$\frac{137 + 2\,(e - 1)}{233} = \frac{x}{y}$$

which simplifies to

$$e = \frac{233\,x}{2y} - \frac{135}{2}.$$

Vapour Densities.—We now come to methods of determining the absolute molecular weights of compounds. Until the last few years the only available method was that of vapour density determination, which we shall take first. Vapour densities may be found either by determining the weight of a given volume of vapour (method of Dumas), or by finding the volume of a given weight (methods of Gay-Lussac, Hofmann, and Victor Meyer). We shall only deal here with Victor Meyer's method. The first exercise will consist in a determination of—

The Vapour Density of Chloroform.—The apparatus necessary consists of burner, water-jacket, vapour-density tube, well-fitting india-rubber stopper for the top, pneumatic trough, graduated tube, glass cylinder, and thermometer. Besides this, a small bulb must be made of glass, with a capillary tube at the end. The method

depends on the rapid volatilisation of the substance, by which means it displaces its own volume of air, which is collected in the graduated tube and measured at the ordinary temperature. Since, whatever be the temperat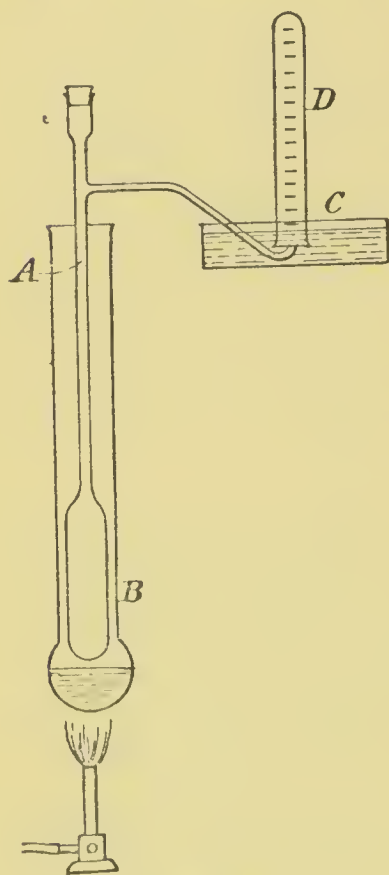ure at which vaporisation takes place, the volume of air displaced is at the same temperature as the displacing vapour, it is not necessary to know the temperature of the tube, for all gases expand at the same rate on heating. The collected air is reduced to 0° C. and 760 mm. pressure, so that we know then the volume which the weight of substance taken would occupy at standard temperature and pressure if it could exist as gas under these conditions.

The first point to attend to is the cleaning and drying of the tube in which the volatilisation of the substance takes place (see A, fig. 37). This consists of a lower cylindrical glass vessel, about 20 cm. long, and with a capacity of about 100 c.cm. The glass tube which is sealed on to the upper end of this is about 60 cm. in length, wider at the top portion. About 50 cm. from where it joins the cylindrical vessel a side tube is fixed on, as shown in the figure. This tube must be first cleansed, rinsed with distilled water, and dried by an air current obtained from bellows or a water-

FIG. 37.

pump.   Whilst the current of air is passed into the bulb the
tube should be gently warmed.   The drying is, in fact,
very similar to that of a tube to be used for nitrogen
estimations.

The outer jacket, B, is now clamped vertically in a
retort-stand, which may be conveniently placed on the
floor near to the working bench.   The leading tube from
the vaporising apparatus, A, will then be at a convenient
height to enter a pneumatic trough, C, which is placed near
the edge of the bench.   The tube, A, should be clamped at
such a height that its position relative to the outer jacket,
B, is that shown in the figure.   The bulb of the water-
jacket is half-filled with water, which is raised to boiling,
so that the cylindrical vessel of the apparatus is heated to
about 100° C.   At the bottom of the tube a small amount
(say 1 cm. in depth) of sand is placed, so that when the
chloroform and its bulb are dropped in, there should be no
chance of breaking the bottom of the apparatus.

About ·15 gram of chloroform is introduced into a
weighed glass bulb having a thin capillary, and the end
sealed.   The bulb and its contents are then weighed again.
Be careful, before doing this, to see that the bulb will pass
easily down the narrow tube of the vessel, A.

Having the water in the bulb of B boiling, and the sealed
bulb with chloroform weighed and ready, we first see if the
apparatus is quite ready for the carrying out of the determi-
nation.   The india-rubber stopper is inserted firmly in the
top of the tube, A, whilst the leading tube is brought under
the surface of water in the pneumatic trough.   If, after half
a minute, no bubbles of air are found to escape from the end
of the leading tube, neither does the water recede up the
leading tube towards A, we may assume that the air inside
A has reached a stage of equilibrium, and is neither

receiving nor parting with heat. A measuring tube, D, full of water, is now brought over the end of the leading tube, the india-rubber stopper removed from the end of the tube A, the end of the capillary broken off (noting, of course, that all the chloroform is in the bulb and none in the capillary), and the bulb and its contents dropped down the tube, the india-rubber stopper being replaced immediately. When the bulb reaches the bottom of the tube the chloroform is volatilised, and its vapour displaces an equal volume of air, the temperature of which is the same as the temperature of its vapour. Bubbles of air consequently escape from the end of the leading tube and collect in the measuring tube, D. After about fifteen seconds no more air will be found to escape. The thumb is then placed firmly under the end of the measuring tube, which is transferred to a cylinder full of water and left there, so that the tube is completely immersed for twenty-five minutes to half an hour. In this way the air in the measuring tube is made to assume the temperature of the water in the cylinder. The volume of air is read off by raising the tube, so that the level of water inside and outside the tube is the same. When taking this reading the thermometer and barometer must be noted.

We now have the data for calculating the vapour density (*i.e.* the density relative to hydrogen) or the specific gravity (compared with air). Let w be the weight of substance taken for the estimation and v the volume of air expelled measured at t°C. and B mm. barometric pressure. Further, let f be the vapour pressure of water at t°. The weight of 1 c.cm. of chloroform vapour at 0° and 760 mm. pressure, if only it could exist as gas under these conditions, would be—

$$\frac{w \times 760 \times (273 + t)}{v \, (B - f) \times 273}.$$

Since 1 c.cm. air weighs ·001293 gram, and 1 c.cm. of hydro-
gen weighs ·0000896 gram under normal temperature and
pressure, we have the following two expressions giving the
specific gravity and the vapour density respectively :—

$$\text{(i.) S.G.} = \frac{w \times 760 \times (273 + t)}{v\,(B - f) \times 273 \times ·001293}$$

and $$\text{(ii.) V.D.} = \frac{w \times 760 \times (273 + t)}{v\,(B - f) \times 273 \times ·0000896}.$$

Other vapour densities besides that of chloroform
should be carried out at a temperature of about 100°;
take, for instance, ether (b.p. 35°), alcohol (b.p. 78°), and
benzene (b.p. 80°·5). In all cases the tube must be care-
fully cleared of all liquid and vapour of a preceding estima-
tion by a current of warm air, and the quantity of substance
taken for the experiment should be roughly calculated so
that not more than about 50 c.cm. of air are expelled.

For estimations of the vapour densities of substances
which have a higher boiling-point than water, it is ne-
cessary to take some liquid other than water to boil in
the outer jacket B—e.g. aniline (b.p. 182°), diphenyl-
amine (b.p. 310°), &c. For temperatures above the
boiling-point of diphenylamine the glass outer jacket is
replaced by a metal case.

Considerable steadiness of temperature may, however,
be obtained by the use of a sand-bath. For this purpose
the cylindrical vessel of the tube, A, is placed in an iron
cylinder about 40 cm. in length, so that its lower portion
does not come nearer than 5 cm. to the bottom end of the
iron cylinder. The space between the two cylinders is
packed with sand, and the bottom of the iron cylinder
heated by a large Bunsen flame. The temperature of
the sand-bath may be approximately ascertained by the

careful use of a thermometer. When this temperature is found to be sufficiently high and constant—ascertained by observing whether the amount of air inside the glass tube, *A*, is undergoing no change—the requisite vapour density determinations can be carried out.

Find, in this manner, the vapour densities of nitro-benzene and naphthalene; the latter, being a solid substance, need not be enclosed within a bulb, but may be melted and then allowed to solidify within a small piece of glass tubing open at both ends, as shown in fig. 38.
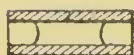
FIG. 38.

Methods depending on the Properties of Solutions.—It will be noted in estimations of molecular weight by the vapour density method that the process is only applicable to such substances as are volatile without decomposition ; since many substances, however, decompose long before they are converted into vapour, methods for the determination of molecular weight by other means are of great importance. Such processes have now been devised. and depend on the properties of solutions ; for an account of the theory of solution the student may be referred to Ostwald's ' Outlines of General Chemistry,' translated by Walker, or ' Solutions,' translated by Pattison Muir ; also to Whetham's ' Solution and Electrolysis.'

Lowering of Freezing-point.—It is a matter of common knowledge that whereas water, if pure, freezes at 0° C., salt water needs to be cooled some degrees below this temperature before freezing sets in ; and that if salt be mixed with snow, much of the latter melts, the temperature sinking at the same time. This phenomenon is by no means peculiar to sea water. It is generally observed that the·freezing-point of any liquid is lowered by dissolving any substance that will dissolve in it. The relations

between the lowering of freezing-point and the amount and nature of the substance dissolved were first studied by Blagden in 1788, and afterwards examined by Rüdorff (1861), and De Coppet (1871). The result of their researches was to show that the lowering of the freezing-point of a solution was proportional to the amount of substance dissolved. In 1882 Raoult proved a most useful general law—viz. that for two equal quantities of one and the same solvent equal lowerings of freezing-point could be effected by dissolving in the two portions, different substances, taken in the proportion of their molecular weights. This may be summed up by saying ' equimolecular solutions have the same point of solidification.' It will be readily seen that this principle can be applied to a method of molecular weight determination, if we take a known weight of some substance, the molecular weight of which is known. Dissolve this in a weighed amount of any particular solvent, and then determine the lowering of freezing-point which is produced. We can very readily calculate how much the freezing-point of 100 grams of the solvent should be lowered by dissolving in it one molecular weight in grams of any substance. This amount is known as the ' molecular lowering of freezing-point ' for the solvent in question. The value varies for different liquids. The following table of constants will be useful :—

Solvent	Constant	$\dfrac{\cdot 02\ T^2}{w}$
Water	18·5	18·9
Formic acid	27·7	28·4
Acetic acid	38·6	38·8
Ethylene dibromide . . .	118	117
Benzene	50	53
Nitrobenzene	70·7	69·5
Phenol	74	76
Naphthalene	69	69·4

In calculating a molecular weight from an experimental result use the figures in the column headed 'constant.' These are the numbers which have been experimentally obtained. The column ' $\dfrac{\cdot 02\,T^2}{w}$,' has been added to show how the molecular lowering can be calculated if one knows for any solvent, T, the melting-point expressed in absolute measure (Centigrade), and w, the latent heat of fusion. The solvent of most general applicability is glacial acetic acid, both on account of its convenient melting-point (17°) and its great solvent action.

Determination of Molecular Weight of Acetanilide.—Having briefly gone over the general principles on which the estimation of molecular weights by the lowering of freezing-point of solutions depend, one can now proceed to an example. The apparatus to be employed is that of Beckmann, the arrangement of which is shown in fig. 39. The solution to be examined is contained in the inner tube, *A*. Note that it contains a thermometer and stirrer passing through a cork in the top, and that it is provided with a side tube also closed with a cork. The stirrer is best made of stout platinum wire, though very little objection can be made to one of rather thin glass rod. The thermometer is of peculiar construction. The length of its scale is only 6° C., each degree is divided into hundredths. So that the thermometer may be of use at different temperatures, the upper end of the capillary is provided with a small reservoir, *a*, into which some of the mercury can be sent by warming the thermometer bulb; and according to the amount of mercury in actual use in the bulb and capillary tube of the thermometer. so it can be used for measurements of differences of temperature

near the freezing-point of various solvents, though in no
case will absolute tempera-
tures be registered.   In
making a molecular weight
estimation we want the
mercury in the capillary
tube to stand somewhere
on the upper part of the
scale, when the tempera-
ture registered is that of
the freezing-point of the
pure solvent. Warm some
water in a beaker until
an accurate thermometer
placed in the water
registers 16·5° to 17° C.
Now introduce the Beck-
mann thermometer into the
water. Should the thread
of the mercury reach to
anywhere between 3 and 6,
no alteration of the mer-
cury contained in the bulb
and capillary is necessary.
On the other hand, the
thermometer may contain
too much or too little mer-
cury for the purpose in
hand.   In the first case
the mercury will reach
above 6, and some must
be removed into the reser-

Fig. 39.

voir, a. In the second case some of the mercury in a must

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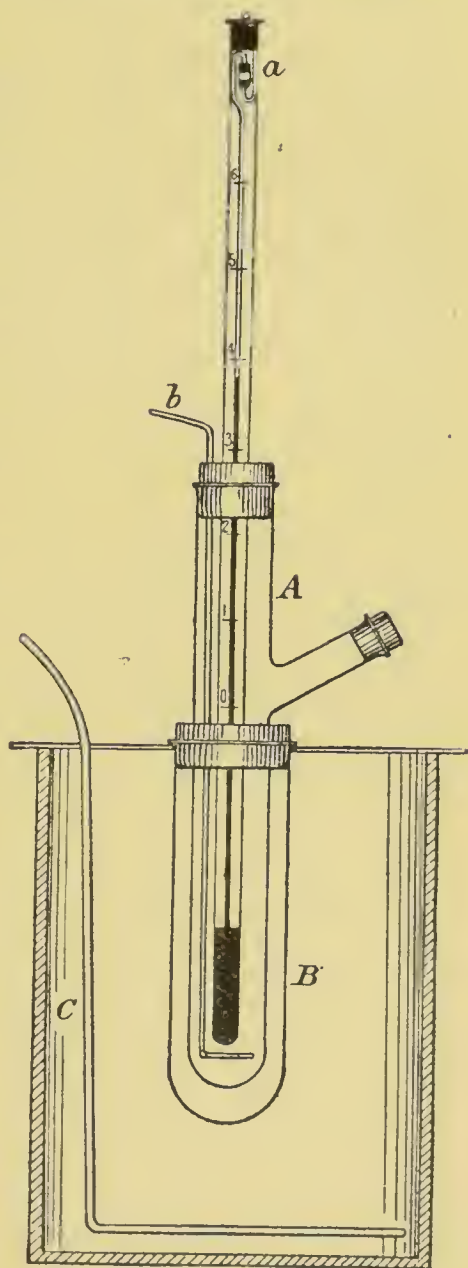
be brought into union with the mercury in the capillary and bulb of the thermometer. In the first case warm the thermometer two or three degrees higher than the temperature at which measurements are to be carried out. Some of the mercury will in this way enter a, and may be detached from the thread by tapping the bulb of the thermometer against the palm of one's hand. The thermometer is then brought back to the temperature at which observations are to be made. If the end of the mercury column now falls on a convenient part of the scale further adjustment is of course unnecessary. It may, however, be necessary to remove more mercury from the capillary to the reservoir, a, in which case the previously described operation is repeated.

In the other case, where mercury has to be removed from the reservoir, a, to the capillary, the thermometer is inverted and tapped gently, so that the mercury of the reservoir is broken up, and some finds its way to the orifice of the capillary of the thermometer. The union of this mercury with that of the capillary is now effected by warming the bulb of the thermometer when the mercury contained therein expands, rises in the capillary, makes its way into the reservoir, a, and uniting with some of the mercury contained in it draws it back with it into the capillary as the thermometer cools. The thermometer is now brought to the temperature at which measurements are to be made, and the convenience or otherwise of the quantity of mercury in the thermometer observed.

We now turn to the other parts of the apparatus. The thermometer and a stirrer, b, made of stout platinum wire or thin glass rod, pass through a well-fitting cork into the vessel, A. The lower part of the stirrer is annular in shape, so that on raising, it surrounds the bulb of the thermometer. The vessel, A, is provided with a side tube also

closed with a cork. This side tube serves for the intro-
duction of substance. The tube, A, which is to contain
the solution, is cooled by water contained in the vessel, C
(provided with a stout stirrer). The water in C does not,
however, come in direct contact with the outside of A ;
the latter tube passes through a cork which in its turn
fits into a tube, B, passing through the metallic lid of the
cooling vessel, C. Hence A is never in direct contact
with the cooling liquid, but is separated from it by the
cushion of air contained in the tube, B.

Remove the thermometer from the tube, A, see that
the latter is perfectly clean and dry, introduce into it two
or three small pieces of platinum foil having sharp corners,
and suspending the tube by wire from a balance, weigh
to the nearest centigram. Now introduce about 15 grams
of pure freshly-distilled glacial acetic acid, taking care
that the sides of the tube are not wetted by the liquid, and
again weigh to the nearest centigram ; the difference of the
two weighings gives the amount of solvent employed.
Replace the thermometer, stirrer, and cork in the tube,
which is then fixed in position in the apparatus. Fill the
outer vessel, C, with water, at about 12° to 13°, *i.e.* three
or four degrees under the melting-point of the solvent.
Work the stirrer in C occasionally, and keep that in A
continually going until the temperature of the acetic acid
is somewhere above its freezing-point. Introduce a very
small crystal of glacial acetic acid into the tube, A ; this is
to induce the solidification of the solvent. Usually it
will be found that the acetic acid is cooled one-tenth of a
degree or more below the freezing-point before solidifi-
cation sets in, but with the crystallisation of the solvent
the temperature rises, attaining a maximum after the lapse
of thirty to sixty seconds, which is taken as the freezing-

point of the pure solvent.   The super-cooling which takes place before the separation of solid solvent sets in has a slight effect on the final temperature noted ; it should, therefore, be kept as small as possible and as far as practicable about the same when the freezing-points of solvent and solution are being determined.

Next allow the acetic acid in the inner tube, A, to become again liquid ; this is most readily attained by removing the tube from the apparatus and immersing it in a beaker containing water at about 20° C.   When the acetic acid has melted, introduce by the side tube about ·2 gram of finely-powdered dry acetanilide from a weighed weighing-bottle, stir so that all is dissolved, and replace the tube, A, and its contents in the apparatus.   Take care not to let the substance stick on the sides of the thermometer, but see that it is dissolved by the acetic acid.   Now weigh the weighing-bottle and remainder of the acetanilide, and make a determination of the freezing-point of the solution in the manner previously described for the pure solvent.   Again melt the acetic acid, add some more acetanilide, and carry out a second determination of freezing-point with the stronger solution so obtained ; a third, and even fourth, determination are better carried out.   When the last determination has been made in the case of the solutions, make a second determination of the freezing-point of the pure solvent as a check on the first determination.   Finally, recover the acetic acid used by distillation.

We now come to the manner of calculating the molecular weight from the observations which have been made. According to Raoult's results, if we write M for the molecular weight of the substance, δt for the observed depression of freezing-point, p for the amount of substance

dissolved in 100 grams of the solvent, and C for the constant of the solvent in question (*i.e.* the amount the freezing-point should be lowered by dissolving a molecular weight of the substance expressed in grams in 100 grams of the solvent), then

$$\frac{M \, \delta t}{p} = C,$$

or of course,

$$M = \frac{C \, p}{\delta t}.$$

C, in the case of acetic acid, is equal to $38 \cdot 6$, whilst p may be replaced by $\dfrac{100 \, a}{b}$, where a is the amount of substance dissolved in a weight of b grams of solvent. This brings the expression to

$$M = \frac{38 \cdot 6 \times 100 \times a}{b \times \delta t}.$$

The results may be conveniently entered in tabular form in the following manner :—

Substance   Examined. — Acetanilide.   Theo.   Mol. Weight.   ~~151.~~   13.5

Solvent Used.—$14 \cdot 35$ grams of glacial acetic acid (b).

Weight of Tube and Substance	Substance in Solution (a)	Observed Melting-point	Observed Depression (d)	Molecular Weight $= \dfrac{38 \cdot 6 \times 100 \times a}{b \times \delta t}$
$8 \cdot 6732$	None	$5 \cdot 82$	None	—
$8 \cdot 4567$	$\cdot 2165$	$5 \cdot 41$	$\cdot 41$	142
$8 \cdot 2362$	$\cdot 4370$	$5 \cdot 01$	$\cdot 81$	145
$8 \cdot 1320$	$\cdot 5412$	$4 \cdot 85$	$\cdot 97$	150

Note particularly in the above table that it is the total amount of dissolved substance and the total depression of freezing-point which is each time brought into the calculation.

A few points as to the application of solvents may be mentioned here. Water serves well for such organic substances which it will dissolve, provided they are of an indifferent character. It has to be remembered here that acids, bases and salts of strong acids or bases, very readily dissociate in dilute aqueous solutions, so that the observed depression is greater and the molecular weight less than that calculated from the formula of the substance. Glacial acetic acid is the most generally useful solvent; one has, however, to remember that it is hygroscopic, and that, therefore, the apparatus must be kept as tightly closed as possible during the operation of determining the lowering of freezing-point of a solution.

Pure benzene is useful in some cases, but care must be taken that it is pure; and it must also be remembered that substances containing hydroxyl groups apparently form molecular complexes when dissolved in solvents which do not themselves contain free hydroxyl. The values obtained for the depression almost always come out too small, whilst the molecular weight deduced from the observations is consequently too high.[1]

Raising the Boiling-point.—If the vapour pressure of any liquid be determined at any given temperature, a certain definite value is obtained if the liquid be pure; but if it contain other substances in solution, then it is found that the vapour pressure of such a solution is less than that of the pure solvent. This means that if a solution be raised to a temperature at which the pure solvent would boil it will not itself enter into ebullition, as at this temperature the pressure of its vapour is not equal to the atmospheric pressure. To make such a solution boil, its temperature

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[1] Compare, however, Auwers, *Berichte*, 1895, **28**, 2878.

must be further increased ; *by dissolving a substance in any solvent the boiling-point of the latter is raised.*

The laws governing the boiling-points of solutions are very similar to those we have occupied ourselves with in the case of the freezing-point being lowered. The amount by which the boiling-point of a solution is raised varies directly with the concentration of the solution, and inversely as the molecular weight of the dissolved substance.

Let M be the molecular weight of the dissolved substance, of which a grams are dissolved in b grams of solvents, and δt the raising of the boiling-point ; then

$$\frac{M \, \delta t \, b}{100 \, a} = C = \frac{\cdot 02 \, t^2}{\omega},$$

where C is a constant depending on t, the boiling-point expressed in absolute Centigrade degrees, and ω the latent heat of the vapour of the solvent. According to Beckmann the following values for t and C may be employed :—

Solvent	Boiling-point	Molecular Raising of Boiling-point
Ethyl ether	34·97	21·1
Carbon disulphide. . . .	46·2	23·7
Acetone.	56·3	16·7
Chloroform	61·2	36·6
Ethyl acetate	74·6	26·1
Ethyl alcohol	78·3	11·5
Benzene	80·3	26·7
Water	100·0	5·2
Acetic acid	118·1	25·3
Ethylene dibromide . . .	131·6	63·2
Phenol	182·3	30·4
Aniline	183·7	32·2

The determination of a molecular weight by the raising of the boiling-point method may be carried out in an apparatus devised by Beckmann. The method has one advantage

over the freezing-point method, that a large number of excellent solvents such as ether, alcohol, carbon disulphide, ethyl acetate, &c., can be employed, since their boiling-points lie at convenient temperatures, whilst their freezing-points are so low as to preclude any practical use being made of them in the freezing-point method.
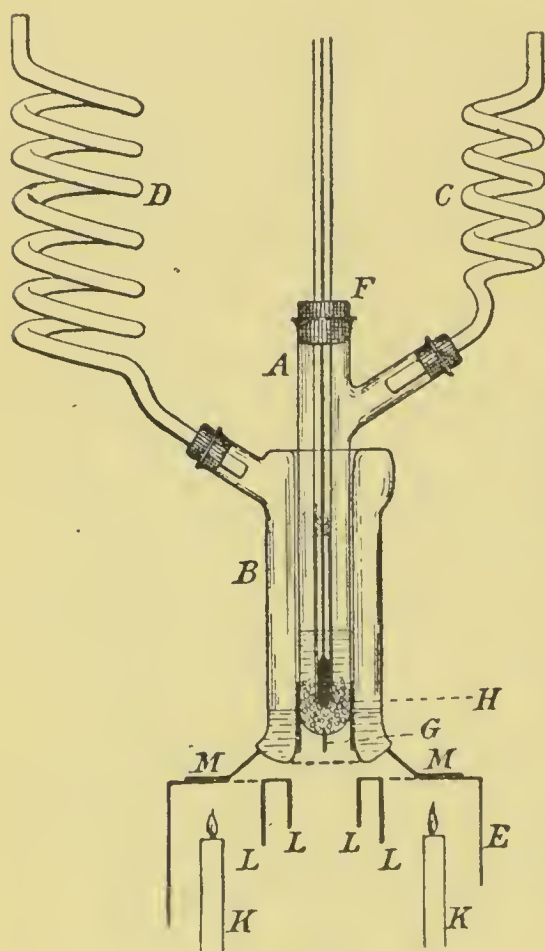
Beckmann has devised two forms of apparatus. A description and sketch (fig. 40) of the later form will be given here, as it possesses advantages. The inner tube, A, contains the solution, the boiling-point of which is to be determined; this is surrounded by a glass jacket, B, which contains about 20 grams of the solvent. Both inner tube and jacket are provided with reflux air condensers, C and D, so that the liquid evaporated is returned immediately.

Fig. 40.

The construction and filling of the inner tube, A, are of primary importance. An adjusted Beckmann thermometer passes through the cork, F; the lower end of its bulb is surrounded with glass beads, which occupy 3 to

4 cm. of the lower end of the tube, A, through the bottom
of which a short piece of platinum wire, G, is fused to
ensure the boiling being regular. The lower end of the
tube, A, is fixed in the outer casing, B, by means of
asbestos paper, H, which is wrapped into a cylindrical
form ; the upper space between the two glass vessels may
be filled with asbestos wool. The boiling of the liquid in
the outer vessel, B, can be aided by the addition of a few
small pieces of porous clay-ware.

The heating of the apparatus is effected indirectly by
placing it on a small box, E, made of asbestos cardboard,
and shown in section in the figure. This box is of
rectangular shape, provided with the raised annulus, $M M$,
for the support of the vapour jacket, and with two rings
shown in section by $L L$, $L L$, which keep off direct heat-
ing by the small flames, $K K$. Indirect heating is further
ensured by having pieces of wire gauze and asbestos paper
just over the positions the burners are to occupy. More-
over, the box is provided with a couple of chimneys,
which, being situated at corners, are not shown in a median
section.

Ether is a very useful solvent on account of its in-
different chemical nature, great solvent power, and ease
with which dissolved substances can be recovered. In
carrying out an estimation the boiling vessel, together
with the glass beads, are weighed. The solvent is then
introduced, and by another weighing the quantity em-
ployed is determined. A determination of the boiling-
point is next made, noting that very small luminous
flames are sufficiently heating when ether is employed.
whilst small Bunsen flames must be used for alcohol. If
ether is employed, the boiling is regulated so that only one
drop of liquid flows back from the air condenser every

three or four seconds ; for alcohol and other higher boiling solvents even more slowly.   Boiling is then effected by means of a slightly larger flame, and the burners so adjusted when the boiling-point is reached that regular, but gentle, boiling goes on.   If the thermometer remains stationary for five to ten minutes, tap it gently at the side, and note the temperature, which may be taken as the boiling-point if it remains constant for a further five minutes.   Without removing the flames the substance is next introduced, the amount taken being exactly determined by weighing.   The first effect will be a lowering of the temperature recorded by the thermometer, but when solution is complete the temperature will again rise, and after some time reach a constant point, which is taken as the boiling-point of the solution.   As in the case of freezing-point determination, one adds further quantities of substance and makes determinations of the boiling-point for several concentrations.   At the end of the series the vessel, A, and its contents are again weighed to see how much solvent has been lost during the process.   This quantity should be as small as possible.

The following points must not be overlooked :—

(a) The height of the barometer.   Read this before and after the series of determinations.   The average effect of 1 mm. difference in the height of the barometer is ·03° in the boiling-point of the solvent.

(b) The concentration of the solution.   The first quantity of substance added should be sufficient to raise the boiling-point about ·2°.   The quantity of substance dissolved is then gradually increased until it forms about 15 per cent. of the solution.

CHAPTER IV

ESTIMATION OF SPECIAL GROUPS OF ATOMS IN ORGANIC COMPOUNDS

CERTAIN groups which are frequently present in organic compounds may be determined by the aid of certain reagents. Generally the process employed results in the formation of a new compound or compounds, one or more of which must then be analysed. Take, for instance, the case of a compound which contains carbon, hydrogen, and oxygen. It is of great importance to know if the oxygen is present in a hydroxylic form or not. We arrive at such knowledge by seeing whether some of the hydrogen can be replaced by acidic groups ; and conclude that each hydrogen atom which can be replaced by an acidic group must be hydrogen, which is linked to the rest of the molecule by oxygen, and is therefore present as hydroxyl.

Again, the amido groups of an acid amide may be estimated by long-continued boiling with an alkali and estimation of the resultant ammonia. On the other hand, amido groups, which are directly united with carbon, cannot generally be eliminated in this way. We shall illustrate these methods by a few examples.

Estimation of Hydroxyl.—The hydrogen of hydroxyl groups can be replaced by acetyl, either by heating with acetic anhydride (with or without the addition of fused sodium acetate), or by treatment with acetyl chloride. The latter compound reacts more energetically, but the

former is frequently preferable as yielding a purer product. Benzoyl groups can be introduced either by boiling with an excess of benzoyl chloride, or by dissolving the substance in dilute alkali and agitating the resulting cold solution with benzoyl chloride. This latter method, due to Schotten and Baumann, is not applicable in the case of acetyl chloride, since the latter decomposes almost immediately when brought in contact with water, forming acetic and hydrochloric acids. The method may, however, be used in the case of benzene-sulphonyl chloride, which resembles benzoyl chloride in some of its properties. We shall illustrate the method by one or two examples.

Estimation of the Hydroxyl Groups in Fluorescein.— This colouring matter occurs in a fairly pure condition in commerce; its formula is $C_{20}H_{12}O_5$. Of these five oxygen atoms, two are present as hydroxyl groups, as may be shown by preparation and analysis of the acetate or benzoate. Weigh out about 10 grams of commercial fluorescein; dissolve it with stirring in about 100 c.cm. of hot water by adding caustic-soda solution in small portions at a time; filter the solution, which possesses a reddish-brown colour when viewed by transmitted light, but by reflected light exhibits a brilliant green fluorescence. Add dilute hydrochloric acid to the filtrate as long as a precipitate is formed; filter off with the aid of a filter-pump, wash the precipitate thoroughly with warm distilled water, and finally transfer the washed and pressed precipitate to a beaker. Dissolve the substance in the least possible quantity of boiling alcohol, filter through a plaited filter into another beaker, warm the contents of the beaker once more to boiling, cover with a glass plate, and allow to cool. The recrystallised fluorescein is filtered off, washed with dilute alcohol, and dried at 100°. A further quantity

of the substance can be obtained by concentrating the filtrate. The formula of the substance has next to be determined by carrying out a combustion. The calculated percentages are $C = 72\cdot29$ and $H = 3\cdot61$.

By acetylation one discovers that only two hydrogen atoms can be replaced by the group $CH_3\cdot CO$—, so that we conclude that only two out of the five oxygen atoms are present as hydroxyl groups.

Weigh out 5 grams of the recrystallised substance into a small round-bottomed flask of about 100 c.cm. capacity. Cover this with 10 c.cm. of acetic anhydride, and fit the flask with a tightly-fitting cork, through which a straight glass tube passes, about 75 cm. in length and of an internal diameter of 6 to 8 mm. Clamp the flask by the neck, and heat its contents over wire gauze until the whole mass becomes liquid. Turn down the flame, so that the liquid boils very gently. The vapours of the acetic anhydride should not rise more than about a third of the way up the tube. The following reaction now takes place :—

$$C_{20}H_{10}O_3(OH)_2 + 2(CH_3\cdot CO)_2O$$
$$= C_{20}H_{10}O_3(OCOCH_3)_2 + 2CH_3\cdot COOH.$$
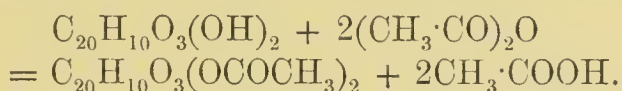
Usually, one hour's gentle boiling is sufficient to convert the fluoresceïn into its diacetyl derivative. The heating should be continued until the original rich brown colour has disappeared and has given place to a greyish shade. Now pour the contents of the flask into a beaker containing a mixture of 40 c.cm. alcohol and 20 c.cm. water. Stir well, and allow to stand about twenty-four hours. Filter off the diacetate which has separated out. Unlike the original substance, it is very sparingly soluble in alcohol. Wash with dilute alcohol by the aid of the

filter-pump. Dry the substance on porous earthenware, dissolve it in a minimal quantity of glacial acetic acid, and precipitate it from this solution by the gradual addition of 80 per cent. alcohol. Filter off the crystalline mass with the aid of the pump, wash with alcohol and then a small quantity of ether, and finally dry at 100°. The substance should now be colourless, and melt at 200°.

The number of acetyl groups which have been introduced into the compound can be readily determined by means of a combustion, which should now be carried out. The introduction of one acetyl group into one molecule of fluorescein lowers the percentage of carbon by 1·7; a second acetyl group effects a further lowering of 1·2 in the carbon percentage. The percentage of hydrogen is, however, but little affected, as seen in the following table:—

		Percentage Composition of		
		$C_{20}H_{12}O_5$	$C_{20}H_{11}O_5(CH_3CO)$	$C_{20}H_{10}O_5(CH_3CO)_2$
C	.	72·29	70·59	69·23
H	.	3·61	3·74	3·85
O	.	24·10	25·62	26·92
		100·00	100·00	100·00

The result of the combustion will, therefore, easily decide for us whether one, two, or more acetyl groups have been introduced into the molecule, and consequently how many of the oxygen atoms are present as hydroxyl groups.

It is easy to see that cases might occur in which the introduction of acetyl groups would be of little use, as the composition of the substance might be such that the replacement of hydrogen by acetyl would not affect the percentage of carbon and hydrogen sufficiently for the ultimate analysis to give us decisive results. A molecular

weight determination would probably, however, enable us to decide by what amount the weight of the molecule had been increased, and consequently how many acetyl groups had been introduced.   An easier way would be, however, to prepare a benzoyl derivative of the substance, since, if the introduction of acetyl in place of hydrogen has but little influence on the percentage composition, the introduction of benzoyl would be almost certain to, on account of the far greater percentage of carbon in this radicle. In the case of fluoresceïn, the preparation of a benzoate would give us the necessary result, since, with the substance in question, the percentage of carbon is materially raised by the introduction of benzoyl.   As indicated above, benzoyl groups might be introduced either by heating the substance with excess of benzoyl chloride, or by dissolving it in dilute soda, adding benzoyl chloride and shaking thoroughly.   A substance containing n hydroxyl groups usually reacts in the following manner when subjected to this treatment :—

$$R(OH)_n + nNaOH + nC_6H_5COCl$$
$$= R(O \cdot COC_6H_5)_n + nH_2O + nNaCl.$$
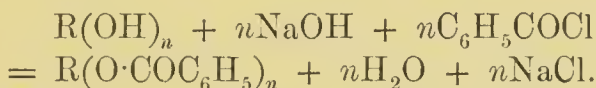
Application of the Schotten-Baumann Reaction to Phenol.—Phenol, C_6H_5OH, may be readily converted into phenyl benzoate, $C_6H_5 \cdot OCOC_6H_5$, by means of this reaction.   Dissolve 1 gram of phenol and $\frac{1}{2}$ gram caustic soda in 10 c.cm. water contained in a well-corked test-tube. Now add $1\frac{1}{2}$ gram benzoyl chloride, insert the cork, and shake energetically until the smell of the benzoyl chloride has completely disappeared.   The phenyl benzoate will very likely separate as an oil, but can be brought to a solid condition by cooling under the tap and rubbing with a glass rod.   It should then be filtered off, washed with

water, dried on a piece of porous plate, and recrystallised from a small quantity of alcohol. (Use a test-tube.) Colourless crystals are so obtained, melting at 68°.

Determination of Methoxyl Groups.—The percentage of methoxyl, CH_3O, contained in a compound can be accurately determined by a method due to Zeisel. This consists in heating the substance with a concentrated solution of hydrogen iodide, when the methyl is split off in the form of methyl iodide.

$$R(OCH_3)_n + nHI = R(OH)_n + nCH_3I.$$

The methyl iodide is conducted into an alcoholic solution of silver nitrate, when silver iodide is produced, which is collected and weighed.

Concentrated hydriodic acid is necessary for this experiment. Zeisel used acid of sp. gr. 1·68 in his experiments.[1] This is about the strongest acid which can be obtained by distillation, and contains 57·7 per cent. of hydrogen iodide (for sp. gr. 1·67).

Hydrogen iodide is obtained by the action of water on phosphorus iodide, or a mixture of phosphorus and iodine. according to the equation—

$$PI_3 + 3H_2O = 3HI + H_3PO_3.$$
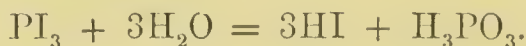
Three grams of red phosphorus and 35 grams of iodine are mixed together in the flask, A. Through the cork of this flask passes a dropping funnel, for introducing 12 to 15 grams of water, and a leading tube which passes into a U-tube, B. This tube is packed with asbestos, which has previously been well dusted over with 3 or 4 grams of red phosphorus, so that the gas, on its way from the generating flask to the vessel in which it is to be absorbed by

water, is brought in contact with phosphorus, which effectually deprives it of any iodine which may be carried over at the same time. The leading tube from the U-tube does not pass directly into the water which is to be used for absorption, since the water might run back on account
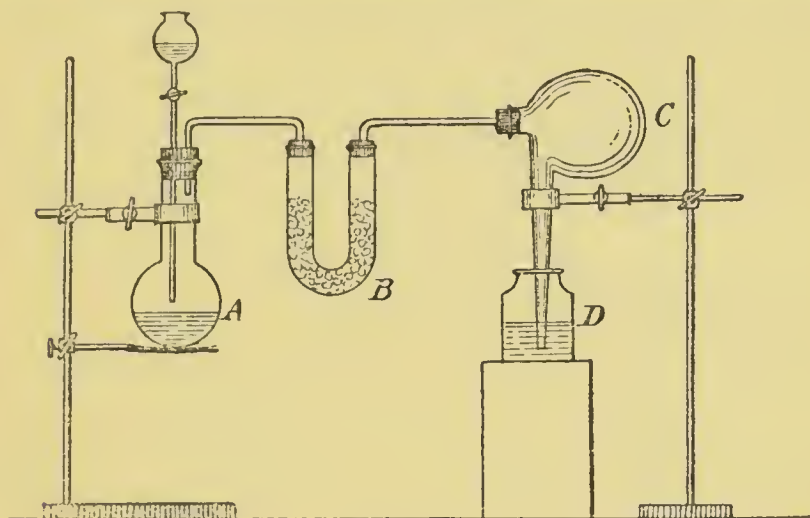
Fig. 41.

of the rapid absorption of the gas, and so spoil the preparation. To avoid this, the leading tube passes through the tubulus of a retort, the neck of which dips into 30 grams of water contained in the vessel, D.

When the apparatus is completely fitted up the water is gradually allowed to drop from the funnel on to the mixture of phosphorus and iodine. At first gas is vigorously evolved; after some time the reaction gets slower, and must be brought to an end by gently heating the contents of the flask, A. The aqueous solution of hydrogen iodide in D is now subjected to fractional distillation. A little water will pass over about 100°. The portion which boils between 125° and 130° is collected apart as concentrated acid.

H

The general arrangement of apparatus for a methoxyl determination is represented in fig. 42. Weigh ·3 gram of brucine (an alkaloid of the formula $C_{23}H_{26}N_2O_4$) which has previously been dried at 105° and then in a desiccator into the flask, A, and cover it with 10 c.cm. of the concentrated hydriodic acid previously prepared. The flask, which is of 30 to 35 c.cm. capacity, has a side tube very similar to that of a boiling-point flask, but directed downwards instead of upwards. Through this side tube a slow stream of washed and dried carbon dioxide is led ; its rate
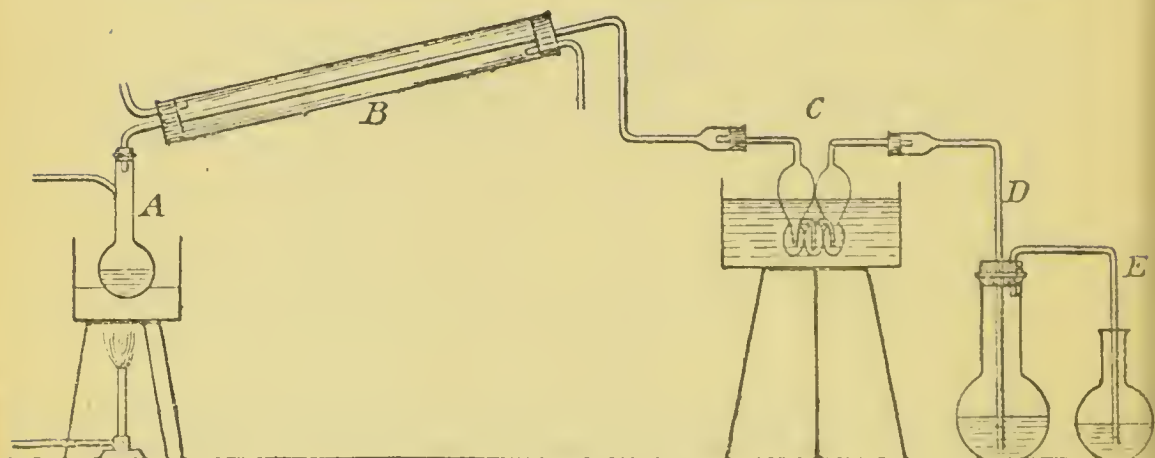
Fig. 42.

should be such that about three bubbles of gas pass the washing bottle in two seconds. The other opening of the flask, A, is connected in the way shown in the figure with an inclined condenser, B, through which water of a temperature of 40° to 45° circulates. The object of this is to condense and return hydriodic acid to A, whilst methyl iodide, which is of low boiling-point, is carried forward. The other end of the condenser leads to a set of potash bulbs, C, which contain water and $\frac{1}{4}$ to $\frac{1}{2}$ gram of red phosphorus. These potash bulbs are kept at 50° to 60° by

means of a water bath.   The issuing gas is passed into a
flask, D, which has a capacity of 80 c.cm., and contains
50 c.cm. of an alcoholic silver nitrate solution.   The last
flask, E, also contains alcoholic silver nitrate ; the quantity
in here is 25 c.cm.   This alcoholic solution of silver
nitrate is prepared by dissolving 2 grams of silver nitrate
in 5 grams of water; after cooling, the solution is filtered
if necessary, and mixed with 45 c.cm. of absolute alcohol.
A solution made in this way must be well stoppered and
kept in a dark place ; it should not be made up too long
before the determination.

All the apparatus being in order and charged in the
way described above, the glycerine bath in which the
flask, A, is placed is heated to 130°, a slow stream of
carbon dioxide being passed through the apparatus.   After
fifteen or twenty minutes' boiling, the liquid in D becomes
clouded, and a precipitate which contains both silver
nitrate and iodide begins to separate out.   The heating
of the flask, A, is continued until the liquid in D becomes
clear, the precipitate settling well ; generally the operation
occupies $1\frac{1}{4}$ to 2 hours, more rarely $2\frac{1}{2}$ hours.   The liquid
in F should show no disturbance even after dilution with
five times its volume of water, and allowing to stand for
several minutes.

This being the case, the liquid and precipitate in D
must be attended to.   The liquid is decanted from the
precipitate into a beaker of about 500 c.cm. capacity.
The precipitate is washed two or three times by decan-
tation with about 30 c.cm. of water each time, and
the washings transferred to the beaker containing the
alcoholic liquid.   The precipitate in the flask becomes
yellow after this treatment, the silver iodide separating
by itself, while the nitrate is removed in solution.   The

precipitate in the flask is then transferred to a small beaker, covered with 20 c.cm. dilute nitric acid, and allowed to stand in a warm place whilst the alcoholic liquid in the larger beaker is being attended to. By diluting the latter with water until the volume reaches about 300 c.cm. the liquid will become somewhat clouded owing to the separation of a small further quantity of silver iodide. Two or three drops of dilute nitric acid are added, and the liquid gently heated until the alcohol is completely evaporated. During this process see that the liquid does not get too concentrated, otherwise some of the silver iodide will be lost. When the smell of alcohol has entirely disappeared water is added until the volume is again brought back to 300 c.cm.; the two quantities of silver iodide are collected on the same filter, well washed, and estimated in the usual manner.

In calculating the results of the analysis remember that 235 parts of silver iodide correspond to 31 parts of methoxyl, CH_3O. Since brucine contains two methoxyl groups, the theoretical percentage of the latter radicle is 15·74.

The method depends on the ease with which methyl iodide reacts with silver nitrate. Most of the halogen compounds of alcoholic radicles do not react in this way; if ethyl bromide is added to silver nitrate not the slightest precipitation of silver bromide takes place.

Estimation of Amido Groups in Acid Amides.—The ammonia of ammonium salts is conveniently and rapidly estimated by distillation with strong caustic potash, when ammonia is expelled and a corresponding potassium salt produced. The equation in such a reaction is that of the general form :

$$NH_4X + KOH = NH_3 + H_2O + KX.$$

(X represents the acid radicle, i.e. Cl, Br, $\frac{1}{2}(SO_4)$, &c.)

The ammonia is received in a known volume of standard sulphuric acid, and the excess of acid titrated after the experiment with standard alkali. This method can be applied in the case of acid amides, since they decompose on prolonged heating with caustic potash, a potassium salt being formed and ammonia eliminated. The reaction in the case of benzamide, $C_6H_5CONH_2$, may be represented by the equation :

$$C_6H_5CONH_2 + KOH = C_6H_5COOK + NH_3.$$

Weigh out ·2 to ·3 gram of dried benzamide into a glass-stoppered retort of 400 to 500 c.cm. capacity ; the end of the neck of this retort should be bent downwards through nearly a right angle, and pass through a well-fitting cork into an absorption bottle of the shape shown in fig. 29. This absorption bottle is charged with 50 c.cm. of deci-normal sulphuric acid, which is used in preference to hydrochloric acid on account of its non-volatility. Pour on to the benzamide a solution which has been made by dissolving 5 grams of stick caustic potash in 50 c.cm. of distilled water. Gradually heat the contents of the retort to boiling, keep the liquid about its boiling-point until the benzamide has entirely dissolved in the potash, and then slowly distil until only about 10 c.cm. of liquid are left in the retort. Care must be taken to avoid splashing or spirting during this operation, since if any potash gets into the sulphuric acid the percentage of ammonia must come out higher than it should.

When all the ammonia has been distilled into the sulphuric acid, the latter is poured into a beaker, the absorption vessel rinsed out a few times with distilled water, and the rinsings added to the remainder of the sulphuric acid. The acid is then faintly coloured by the

addition of methyl orange and the free sulphuric acid
titrated with decinormal soda or sodium carbonate.

If x c.cm. of soda are necessary to effect neutralisation,
$50 - x$ c.cm. of the acid must have combined with am-
monia. The quantity of ammonia which has been obtained
from the benzamide is therefore $(50 - x) \times \cdot 0017$ gram,
which has been obtained from $(50 - x) \times \cdot 0016$ gram of
amidogen, NH_2. Calculate your result as percentage of
amidogen, NH_2, in benzamide.

Nitriles of acids are also decomposed on boiling with
an alkali according to the equation :

$$R \cdot CN + KOH + H_2O = R \cdot COOK + NH_3.$$

On account of the volatility of most nitriles, very inaccu-
rate results would be obtained if an attempt were made to
hydrolyse them by the process described in the case of
benzamide. A complete hydrolysis can, however, be
effected by heating with fuming hydrochloric acid in a
sealed tube (generally speaking to 100° or 120°); aceto-
nitrile furnishes in this way acetic acid and ammonium
chloride as follows :

$$CH_3CN + HCl + 2H_2O = CH_3 \cdot COOH + NH_4Cl.$$
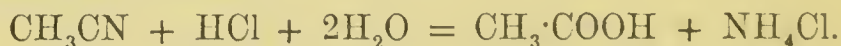
The ammonia can now be readily estimated by trans-
ferring the contents of the tube to a retort, rendering
alkaline with caustic potash, and distilling off the ammonia
which is received in standard acid.

PART II

CHAPTER V

COMPOUNDS OF THE FATTY SERIES

SECTION I.—THE HYDROCARBONS

THESE compounds of carbon and hydrogen may be divided into two groups, saturated and unsaturated hydrocarbons. In the first of these groups the carbon atoms are united to one another by single linkages, in the latter double or treble linkages exist between pairs of carbon atoms. This difference in the linkage conditions a difference in chemical behaviour; whereas saturated hydrocarbons can only give rise to new compounds by a process of substitution, the unsaturated hydrocarbons very readily unite with certain elements and groups forming addition products. This is exemplified by the reaction of the two hydrocarbons methane, CH_4, and ethylene, C_2H_4, with chlorine. The former gives methyl chloride, CH_3Cl, one atom of hydrogen being replaced by one of chlorine according to the equation:

$$CH_4 + Cl_2 = CH_3\,Cl + HCl.$$
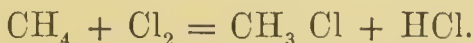
In the case of the other hydrocarbon, one molecule of

ethylene unites with one molecule of chlorine to form ethylene dichloride, $C_2H_4Cl_2$:

$$C_2H_4 + Cl_2 = C_2H_4Cl_2.$$
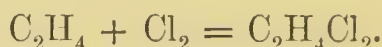
1. **Preparation of Methane.**—This gas, the simplest of the hydrocarbons, is most readily prepared by heating a mixture of fused sodium acetate with soda-lime :

$$CH_3{\cdot}COONa + NaOH = CH_4 + Na_2CO_3.$$

Weigh out 70 grams of the crystallised sodium acetate, which contains 3 molecules of water of crystallisation. Heat this in a dish of iron or nickel over a small Bunsen flame, stirring the substance continually with a glass rod. The salt will soon melt, and by continuing the heating the water of crystallisation may be expelled. The heating must be cautiously conducted, as the expulsion of the water from the fused mass is accompanied by considerable spirting unless due care be exercised. Towards the end of the process the temperature may be increased, the anhydrous salt having a melting-point of 319°. When all symptoms of boiling disappear, the dish and its contents may be allowed to cool, the sodium acetate solidifying to a pearly-looking mass. This is then removed from the dish, weighed (about 40 grams of the fused mass will be obtained), and ground up in a mortar with twice its weight of soda-lime.

Next choose a round-bottomed hard glass flask of such a size that the mixture of acetate and soda-lime will approximately occupy one-third of the bulb. Choose a well-fitting cork for the neck of the flask, bore one hole through it, and connect by a leading tube with a moderately-sized washing bottle containing a solution of sodium hydroxide. This must be connected in turn with

a second washing bottle, charged with concentrated sulphuric acid. From the second washing bottle the gas will have to be led by a tube to a pneumatic trough, so that it may be collected over water.

The apparatus being set up and connected, the heating may be begun. The hard glass flask is clamped at the neck, and heated by a moderately large Bunsen flame, which is kept in circular motion so as to attain an equable heating of the flask and its contents. Gas will soon be evolved, and, as in all preparations of this kind, the regulation of the flame should be carefully attended to, so that the evolution of gas should not be too violent. From time to time fill test-tubes with the issuing gas, and as soon as the issuing gas is found to burn quietly without explosion on applying a light, collect four or five jars of methane over the beehive shelf. The contents of these jars may then be used for the following experiments :—

(i.) Remove a jar of the gas from the pneumatic trough and, holding it with the open end downwards, plunge a lighted taper up into the gas. The gas at the mouth of the jar will be ignited and burn with a slightly luminous flame, the taper as it passes into the jar beyond the flame being extinguished.

(ii.) That methane is lighter than air may be proved by pouring it upwards from one jar into another. As it rises into the second jar, it naturally becomes mixed with air, the mixture thus formed exploding on applying a light. A mixture of methane with double its volume of oxygen is extremely explosive, more so even than electrolytic gas.

(iii.) Mix methane with its own volume of chlorine. This must be done in diffused light, since exposure of such a mixture to direct sunlight brings about an explosion. Such a mixture will, after a time, lose its smell of chlorine,

an ethereal odour, due to the formation of chlorine substitution derivatives, taking its place.

The methane prepared by the above process is never pure. Not only is this gas evolved when sodium acetate is heated with an alkali, but a certain amount of ethylene and hydrogen are produced at the same time. The former gas is removed by the washing bottle containing the strong sulphuric acid, but there is no simple method for separating the methane and hydrogen. The action of the alkali is virtually the removal of the elements of one molecule of carbon dioxide from one molecule of acetic acid:

$$CH_3 \cdot CO_2H - CO_2 = CH_4.$$

The reaction is frequently made use of; sometimes, instead of soda-lime, barium or calcium oxides are used to effect the removal of carbon dioxide, whilst in certain cases simple heating of a carboxylic acid is sufficient.

To obtain perfectly pure methane, zinc-methyl is decomposed by water:

$$Zn(CH_3)_2 + 2H_2O = 2CH_4 + Zn(OH)_2.$$
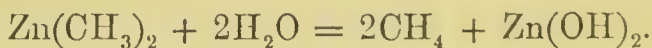
An interesting synthetical method for the formation of methane was discovered by Berthelot, who led a mixture of sulphuretted hydrogen and the vapour of carbon disulphide over red-hot copper:

$$CS_2 + 2H_2S + 8Cu = CH_4 + 4Cu_2S.$$
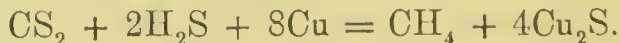
The following general methods of the formation of paraffins, i.e. hydrocarbons of the general formula C_nH_{2n+2}, may be mentioned:

Frankland heated an alkyl iodide with zinc to 150°:

(a) $2Zn + 2C_2H_5I = Zn(C_2H_5)_2 + ZnI_2.$
(b) $Zn(C_2H_5)_2 + 2C_2H_5I = 2C_4H_{10} + ZnI_2.$
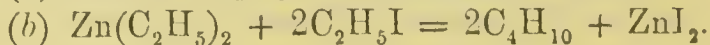
Wurtz's method consists in the action of sodium on alkyl halogen compounds at lower temperatures. With a mixture of ethyl and amyl iodides the following three reactions will take place :

$$2C_2H_5I + 2Na = C_4H_{10} + 2NaI.$$
$$C_2H_5I + C_5H_{11}I + 2Na = C_7H_{16} + 2NaI.$$
$$2C_5H_{11}I + 2Na = C_{10}H_{22} + 2NaI.$$
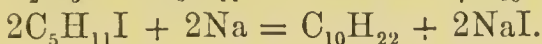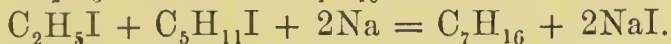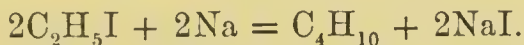
The halogen derivatives of the hydrocarbons may be converted into the hydrocarbons themselves by various reduction processes, *e.g.* with a copper-zinc couple (Gladstone and Tribe) :

$$CH_3I + 2H = CH_4 + HI.$$
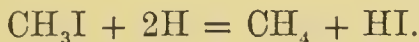
Kolbe electrolysed the fatty acids ; diisobutyl is formed, for example, from valeric acid :

$$2C_4H_9COOH = C_8H_{18} + 2CO_2 + H_2.$$

2. **Preparation of Ethylene and Ethylene Dibromide.**— Ethylene is most easily prepared by heating alcohol with strong sulphuric acid. The net result of the reaction which takes place is that the alcohol is deprived of the elements of water. Mix 25 grams of alcohol and 150 grams of strong sulphuric acid in a flask of two or three litres capacity. Fit the neck with a cork, through which bore two holes, one for a stoppered dropping funnel, the second for a leading tube which passes to the first of two washing bottles. The flask, which is clamped by the neck, is supported on wire gauze so that the subsequent heating should not be direct. The washing bottles are arranged so that the gas must pass through them in succession, the first being charged with concentrated sulphuric acid to remove the vapours of alcohol and ether, the second with

canstic soda solution to hold back carbon dioxide, and towards the end of the experiment sulphur dioxide. Further, mix alcohol and concentrated sulphuric acid separately in a beaker, 25 grams of the former and 50 grams of the latter.

Before warming the contents of the flask and attempting to collect any of the ethylene which is evolved, get ready the apparatus for the absorption of the gas by bromine, so that the operation of heating the flask may be carried on continuously and need not be broken whilst the bottles are being charged and connected. To absorb the ethylene by bromine, fit up the following washing bottles so that the gas must pass through them in the following order : (i.) an empty washing bottle, (ii. and iii.) two washing bottles, the one next to the empty bottle containing 60 grams of bromine covered with a depth or 1 cm. of water, the second with 40 grams of bromine similarly covered with water. Place the latter in a dish so that it may be cooled by water from the outside during the absorption process. The tube leading from the bromine absorption bottles must not open directly into the air, but should go to the bottom of a lime-tower, which is charged from the constriction upwards with alternate layers of broken glass and soda-lime. The function of this tower is to absorb any bromine vapour which may be carried over.

Everything being ready, the heating of the flask containing the sulphuric acid and alcohol may be begun. When a continuous supply of ethylene begins to come off, run in the mixture of one part of alcohol and two parts of sulphuric acid through the dropping funnel at such a rate that the supply of gas is continuous. Test the issuing gas occasionally by collecting a test-tube full and noting

whether it burns with a steady flame or whether it explodes ; when the gas is being evolved in a fairly pure condition, collect a jar or two over the pneumatic trough, and then, disconnecting the leading tube, connect the washing bottles with the previously prepared bromine-absorption apparatus.

With the gas that has been collected, note that it will burn with a luminous flame and forms a violently explosive mixture with air.

Pass the ethylene into the 100 grams of bromine ; that in the first vessel will lose its dark brown colour first ; and continue the current of gas until the liquid in the second washing bottle also assumes a pale yellow colour. Disconnect the bottles, transfer the two quantities of ethylene dibromide to a separating funnel, and wash thoroughly by shaking with a dilute solution of caustic soda. Then separate the heavier dibromide from the aqueous layer and wash again twice, but this time with water. Finally separate the ethylene dibromide as completely as possible from the water, running it into a flask. Add calcium chloride to the contents of the flask, cork well and agitate from time to time. Pour the ethylene dibromide from the calcium chloride into a boiling-point flask and submit it to fractional distillation (see fig. 6). Collect the portion that comes over between 128° and 131°. (The boiling point is 129·5°.)

3. **Preparation of Acetylene** (C_2H_2). — Thoroughly clean out and dry a flask of 300–400 c.cm. capacity. Fit it with a cork, through which bore two holes, one for the introduction of a dropping funnel, the other for a tube leading to a washing bottle. Half fill the washing bottle with water and connect with a leading tube to a small pneumatic trough. Introduce into the generating flask

about 20 grams of calcium carbide—a compound formed
by heating lime and carbon in the electric furnace—and
pour water into the dropping funnel, taking care that the
cock is shut off and that no water reaches the carbide,
otherwise evolution of gas will at once begin.   The appa-
ratus being arranged, drop water very slowly drop by drop
on to the calcium carbide.   As each drop reaches the car-
bide, evolution of gas occurs, the carbide crumbling to a
powdery mass of calcium hydroxide.   Collect test-tubes of
gas occasionally and test the purity of the acetylene by
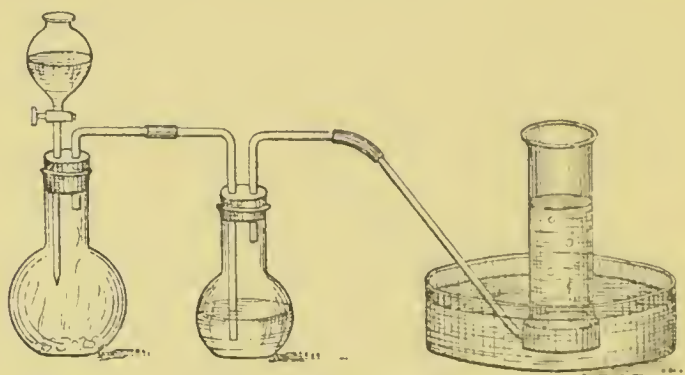
FIG. 43.

applying a light.   As soon as the gas burns quietly without
an explosion, allow the water from the funnel to go on
dropping slowly on to the carbide until two or three jars
of gas have been collected.   Turn off the cock of the sepa-
rating funnel, and with the contents of the jars perform
the following experiments :—

(i.) Take off the ground-glass plate from one of the jars
and apply a light.   The acetylene burns with a smoky, very
luminous flame.

(ii.) From another jar remove the cover rapidly, pour in
about 10 c.cm. of concentrated sulphuric acid, and rapidly

replace the cover, which should be sufficiently greased and fit quite air-tight. Shake up the contents of the jar, and stand it aside for a few hours. It will then be found that there is a diminution of pressure of the gas inside the jar, owing to its partial absorption by the sulphuric acid.

(iii.) Now pour into a test-tube a few c.cm. of bromine and cover this with water to the depth of 1 cm. Introduce the end of the leading tube under the surface of the bromine, and by allowing water to drop on the calcium carbide evolve more gas. The bromine will be decolourised after the acetylene has been passed into it for a few minutes.

(iv.) In another test-tube boil 2 or 3 c.cm. of concentrated hydrochloric acid with a small amount of copper oxide until the latter is dissolved. Add a few copper turnings and boil again until the green colour of the cupric solution has been discharged. Pour off the clear liquid to another test-tube, and add ammonia cautiously. When the liquid is nearly neutralised cuprous chloride will be precipitated ; the ammonia should be added until this precipitate just redissolves. On passing acetylene into this solution a dark red precipitate of copper acetylide is obtained.

In carrying out these experiments with acetylene, be careful not to let the gas escape more than possible. Acetylene has a peculiarly unpleasant smell and is poisonous.

Many other metallic carbides yield acetylene when treated with water ; the reaction being similar to that which takes place in the case of calcium carbide :

$$C_2Ca + 2H_2O = C_2H_2 + Ca(OH)_2.$$
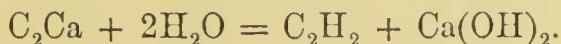
Previous to the commercial production of calcium

carbide on the large scale, the gas was usually prepared by the action of alcoholic potash on ethylene dibromide. The gas evolved was in this case first passed through a reflux condenser to return the volatilised alcohol, and then through a second flask, also provided with a reflux condenser and containing boiling alcoholic potash, to decompose the bromethylene formed at the same time as far as possible. The reactions taking place are expressed by the equations :

$$CH_2Br \parallel CH_2Br + KOH = KBr + H_2O + CH_2 : CHBr.$$
$$CH_2 : CHBr + KOH = KBr + H_2O + CH : CH.$$
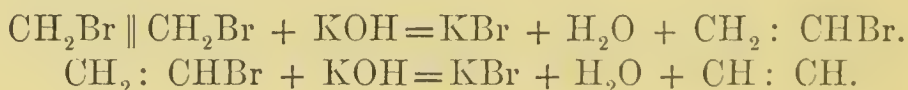
Acetylene is also formed by the electrolysis of fumaric acid :

$$\begin{matrix} HOOC \cdot CH & & CH \\ \parallel & & \parallel\parallel \\ HC \cdot COOH = & & CH + 2CO_2 + H_2 \; ; \end{matrix}$$
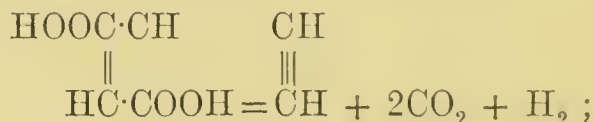
and by the incomplete combustion of ethylene. It is the formation of acetylene in this way which produces the unpleasant smell when the flame of a Bunsen burner strikes back to the small gas jet. The acetylene thus produced can be isolated by aspirating the gases from the Bunsen burner through an ammoniacal solution of cuprous chloride, and afterwards heating the cuprous acetylide with strong hydrochloric acid :

$$C_2H_2 + CuCl + NH_3 = C_2HCu + NH_4Cl.$$
$$C_2HCu + HCl = C_2H_2 + CuCl.$$
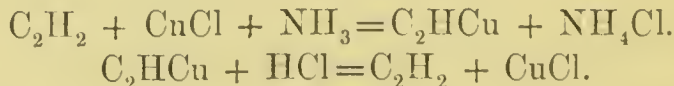
When acetylene is absorbed by concentrated sulphuric acid, and the liquid subsequently distilled with water, crotonaldehyde is formed. Probably acetaldehyde is first produced : this then undergoes the aldol condensation, and

finally by the splitting off of water crotonaldehyde is formed :

$$CH : CH + H_2O = CH_3 \cdot CHO.$$
$$2\ CH_3 \cdot CHO = CH_3 \cdot CH(OH) \cdot CH_2 \cdot CHO.$$
$$CH_3 \cdot CH(OH) \cdot CH_2 \cdot CHO = CH_3 \cdot CH : CH \cdot CHO + H_2O.$$
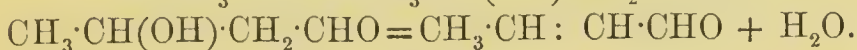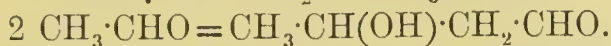
Bromine absorbs acetylene with production of acetylene tetrabromide, not however in the pure condition :

$$CH : CH + 2Br_2 = CHBr_2 \cdot CHBr_2.$$
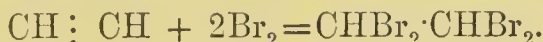
Section II.—The Alcohols

The alcohols, many of which are formed during processes of fermentation, may be divided into three groups— (a) primary alcohols (of the general formula $R \cdot CH_2OH$), (b) secondary alcohols ($RR' \cdot CHOH$), and (c) tertiary alcohols ($RR'R'' \cdot COH$). These different classes of alcohols may be distinguished by their different behaviour on oxidation, and also by conversion into nitroparaffins. When a primary alcohol is oxidised an aldehyde is first formed, and this by further oxidation passes into an acid containing the same number of carbon atoms as the original alcohol. A secondary alcohol first gives a ketone containing the same number of carbon atoms as the alcohol, whilst further oxidation effects a breaking up of the molecule, acids containing a smaller number of carbon atoms than the original alcohol being formed. In the case of the oxidation of tertiary alcohols the molecules of the latter are at once broken up. The changes on oxidation may be illustrated by the following equations in the case of ethyl and isopropyl alcohols :

$$CH_3 \cdot CH_2OH + O = CH_3 \cdot CHO + H_2O.$$
$$CH_3 \cdot CHO + O = CH_3 \cdot COOH.$$
$$CH_3 \cdot CHOH \cdot CH_3 + O = CH_3 \cdot CO \cdot CH_3 + H_2O.$$

I
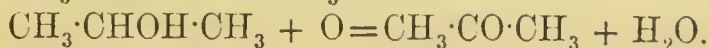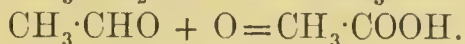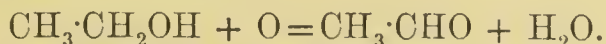
The method of finding out the nature of an alcohol (*i.e.* whether it is primary, secondary, or tertiary) by conversion into nitroparaffins will be illustrated in subsequent preparations.

4. **Preparation of Ethyl Iodide** (C_2H_5I).—Weigh into a small flask 4 grams of red phosphorus and 20 grams of alcohol (90 % alcohol is strong enough for this preparation). The flask should be provided with a sound cork (not an india-rubber stopper), through which a reflux condenser is passed. The arrangement of tubes for passing water first through the condenser and using the water afterwards for the feeding of the water-bath on which the flask and its contents have afterwards to be heated is shown in fig. 44. Add to the mixture of red phosphorus and alcohol contained in the flask, 40 grams of iodine in small quantities at a time. When all the iodine has been added the flask and its contents should be allowed to stand without heating for twenty to twenty-four hours. At the end of this time the water-bath can be heated and the mixture boiled gently under reflux (water being run through the condenser to keep it cool) for half an hour. Then allow the flask and its contents to cool, remove the condenser
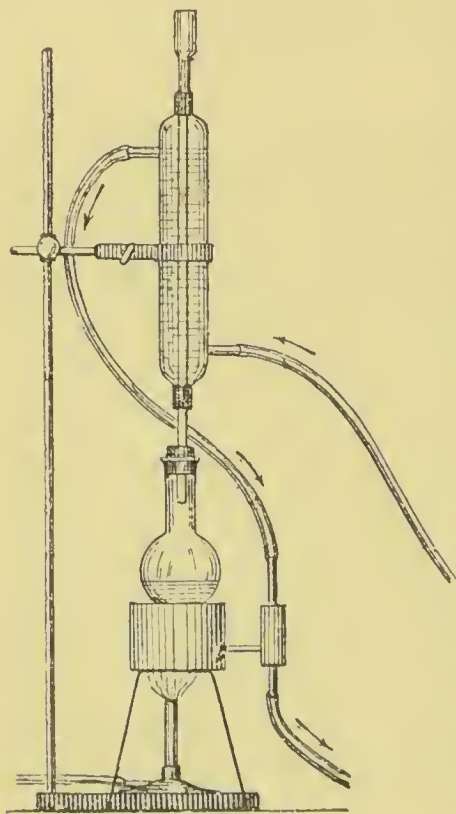
Fig. 44.

from the position it is in, and arrange it in a slanting
position so that it can be used for distillation. Connection
is made between the flask and the condenser by inserting
through the cork of the former a bent piece of glass tubing
which also passes through a cork in the upper, wider end
of the condenser (see fig. 45). The liquid contained in
the flask is then distilled
over as completely as
possible by the aid of the
water-bath, the distillate
being received in a small
flask. The crude ethyl
iodide is then transferred
to a separating funnel
and washed, first with a
dilute solution of caustic
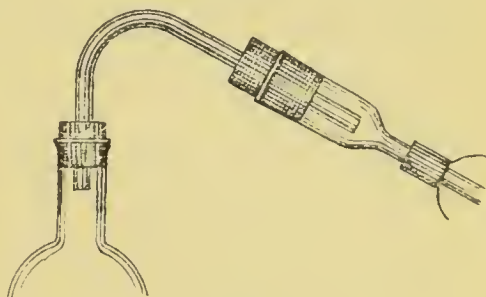
Fig. 45.

soda and then with water. Finally, the liquid is separated
from the water, dried over calcium chloride, and fractionated
as in the case of ethylene dibromide. Boiling point 72°;
yield rather more than equal to the weight of iodine
employed. The theoretical yield is 49 grams.

Add a few drops of ethyl iodide to 2 c.cm. of water
contained in a test-tube. Shake up; the ethyl iodide does
not dissolve but sinks to the bottom of the water. Now
add a few drops of silver nitrate solution, and shake again.
It will be noted that silver iodide is precipitated. Usu-
ally the halogen derivatives of the hydrocarbon do not so
readily precipitate silver nitrate solution; the correspond-
ing ethyl bromide has to be raised to a boiling temperature
before it will yield silver bromide.

The reaction which takes place between phosphorus,
alcohol, and iodine is expressed by the equation :

$$P + 5C_2H_5OH + 5I = 5C_2H_5I + H_3PO_4 + H_2O.$$

The alcohol and phosphoric acid react, however, with one another, forming ethyl-phosphoric acid, which is left in the flask when its contents are distilled on the water-bath; it is on account of this reaction that more than the theoretical amount of alcohol must be taken.

Determination of the Density of Ethyl Iodide.—A very important physical measurement in the case of liquids is the determination of the density, numerically equal to the specific gravity if compared with the weight of an equal volume of water at $4°$, the temperature at which this standard liquid has its maximum density. The determination of the density of some organic liquid should be carried out, and this may very well be done with the ethyl iodide just prepared. The determination is usually made by weighing a vessel (pyknometer) when empty (really when filled with air, for which a correction is made if accurate results are desired), then weighing it full of the liquid in question, and finally with distilled water. If w, w', and w'' be the three weights obtained, the density, D, will be obtained from the formula:

$$D = \frac{w' - w}{w'' - w};$$

Fig. 46.

to which various corrections will have to be applied for temperature, density of air, &c., if an accurate result is desired.

Pyknometers are of various forms, as illustrated by figs. 46, 47, and 48.

A simple form is shown in fig. 46; it consists of a small flask, usually of about 25 c.cm. internal capacity, into the neck of which a glass stopper provided with a central capillary tube has been carefully ground. The pyknometer is first weighed empty

after it has been carefully dried. (The drying may be
effected by rinsing out the interior, first with alcohol,
then with ether, and finally aspirating a current of air
through the bottle.) The bottle is then filled with the
liquid whose specific gravity is to be determined, care
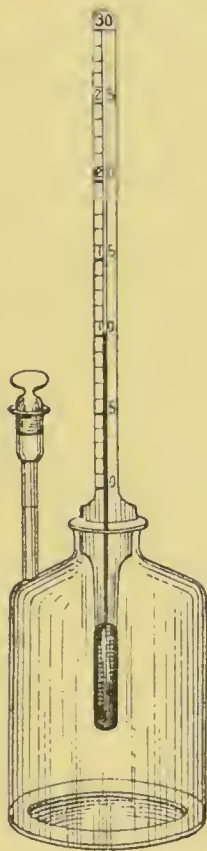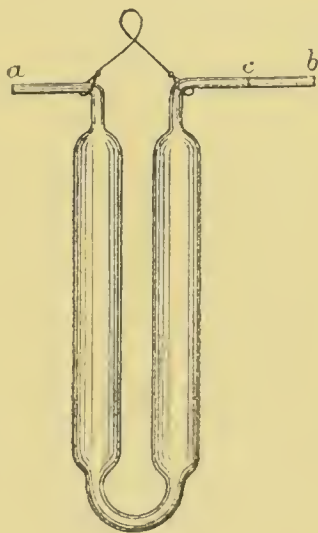
FIG. 47.   FIG. 48.

being taken that no bubbles of air are left inside the
bottle. The stopper is then inserted; some of the liquid
will escape over the neck of the bottle, the rest of the
surplus being forced up the capillary tube. Then see
again that the bottle and capillary tube are absolutely
full of the liquid, and that no bubbles of air have been left.

Wipe off the liquid which has collected round the neck of the bottle and at the end of the capillary tube, and weigh the bottle and its contents accurately. The bottle is then emptied, rinsed out, and filled with distilled water in the way described for the liquid; then the third weighing is taken. The temperature both of the liquid and the water should be determined immediately before filling the pyknometer, and the weighings then carried out as soon as possible.

A more elaborate form of pyknometer is represented in fig. 47; the stopper is replaced by a thermometer, which acts in the same capacity, and on insertion forces liquid up the side tube. The excess of liquid in this side tube above a certain engraved mark is removed by porous paper; the weighings are carried out as described for the simpler pyknometer.

The density of liquids can be most accurately determined by means of Sprengel's pyknometer, represented in fig. 48. This instrument consists of an U-tube terminated at either end by horizontal capillary tubes, over which ground-glass caps fit. One of the horizontal capillary tubes has a mark, c, on it; the apparatus is suspended from the balance by means of platinum wire. The internal content of the pyknometer is from 5 to 20 c.cm. In filling the tube, a piece of india-rubber tubing is attached to the end a, the end b being immersed in the liquid. The tube is then completely filled with liquid by sucking at the end of the india-rubber tube, care being taken that no bubbles of air are left in the apparatus. The pyknometer is then set in a water-bath, regulated carefully by a thermostat so that the liquid may be brought to a definite temperature, the only part of the pyknometer which is not immersed being the two narrow horizontal

tubes. After ten minutes the liquid in the pyknometer
will have attained the temperature of the water-bath.
Before removing the pyknometer for weighing, it is
necessary to see that when the liquid occupies the whole
of the tube a, that it only comes as far as the mark, c, on
the tube b. Should there be too much liquid in the tube
b, hold a piece of filter paper to the end a, by which some
of the liquid can be easily withdrawn. If, on the other
hand, there is too little liquid in b, hold a drop of liquid on
the end of a glass rod to the orifice at a—the drop will be
drawn by capillarity into the tube. When the liquid has been
brought to such a volume that it entirely fills the tube
from the orifice of a to the mark c, any liquid on the
exterior of these tubes is carefully removed, the two caps
fitted on, the pyknometer removed from the water-bath
and carefully dried on the outside. During this operation
do not warm the pyknometer with the hand unnecessarily,
otherwise the liquid will expand, and some may pass into
the glass caps; such an occurrence should be carefully
avoided. The weighing is then made; three weighings
are necessary as with the other forms of pyknometer—$i.e.$
when the instrument is filled respectively with air, water,
and the liquid whose specific gravity is to be determined.

We will suppose that we wish to find the density of
the liquid referred to water at $4°$, and that the weighings
when made with liquid and water were at the same tem-
perature, t.

Then

$$D = \frac{w' - w}{w'' - w} (\Delta - ·0012) + ·0012,$$

where D is the density of the liquid, w, w', and w'' are the
weights of the pyknometer when uncharged, full of the

liquid, and full of water respectively, Δ is the density of water at $t°$, and $\cdot0012$ is the density of air referred to that of water. Should the water and the liquid with which the pyknometer was filled have been at different temperatures, t_w and t, then another correction must be applied for the cubic coefficient of expansion of the glass; the coefficient may be taken at $\cdot000025$ per degree. This alters the formula to

$$D = \frac{w' - w}{w'' - w} \times [1 + \cdot000025\,(t_w - t)] \times [Q - \cdot0012] + \cdot0012,$$

where Q is the density of water at the temperature in question. For any accurate determinations in which the fifth decimal place is required correct, use $\cdot00119$ instead of $\cdot0012$ for the density of air.

Linnemann gives the specific gravity of ethyl iodide as $1\cdot9444$ at a temperature of $14\cdot5°$.

5. **Preparation of Isopropyl Alcohol from Acetone.**—Not only may ketones be prepared from secondary alcohols by a process of oxidation, but, by a reversal of the reaction, ketones can be reduced to secondary alcohols. The reaction may be carried out in the case of acetone, which is reduced by nascent hydrogen (from sodium amalgam and water) to isopropyl alcohol :

$$CH_3 \cdot CO \cdot CH_3 + 2H = CH_3 \cdot CH(OH) \cdot CH_3.$$
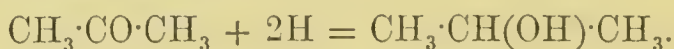
Place 750 grams of clean mercury which has been thoroughly dried in a fairly large porcelain dish. The complete drying may be effected by heating the mercury in the dish gently for some time, say to $150°$, and then allowing it to cool. Both the heating of the mercury and the subsequent operation of making the sodium amalgam must be done in a draught cupboard. A stout piece of

glass rod about 70 cm. in length is drawn out at one end to a sharp point, and this pointed end bent down as shown in the figure. Now cut up 25 grams of sodium into slices about the size of a shilling, spit one of these pieces on the pointed end of the glass rod, and depress it quickly under the surface of the mercury. The first few pieces which are introduced in this way catch fire on coming in contact with the mercury, and a small amount of metal is always thrown
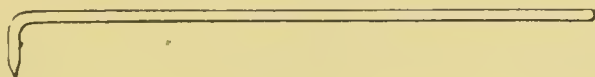
FIG. 49.

out. Great care must therefore be taken—it is as well to put on gloves and spectacles when making sodium amalgam. Afterwards, the introduction of the sodium can be effected more quickly; in fact, if the operation takes place too slowly, the amalgam cools and solidifies. When all the sodium has been added allow the amalgam to cool and then break it up into pieces of a convenient size and transfer immediately to a well-corked bottle.

Weigh out 20 grams of acetone and 100 grams of water and transfer to a stout glass bottle of 300 or 400 c.cm. capacity; this is to be provided with a good cork. Now add the sodium amalgam in small portions at a time and agitate frequently. As the sodium goes into solution, the mercury becomes liquid; proceed with the addition of the amalgam until fresh quantities, when introduced, give rise to a considerable evolution of hydrogen. Then pour off the liquid from the mercury, and distil from a boiling-point flask all that comes over below 95°. Add ignited potassium carbonate to the distillate; the bottle in which it is contained is thoroughly corked and allowed to stand

over night. Then distil off the isopropyl alcohol, which, in order to effect complete dehydration, is then allowed to stand for some time with half its weight of fused caustic potash. Another distillation furnishes the isopropyl alcohol as a colourless liquid of boiling-point 83°–84°, miscible with water in all proportions.

During this preparation a certain amount of the acetone gets reduced in a different manner, tetramethylethylene glycol (a pinacone) being produced :

$$2\frac{CH_3}{CH_3}{>}CO + 2H = \frac{CH_3}{CH_3}{>}C(OH) - C(OH){<}\frac{CH_3}{CH_3}.$$
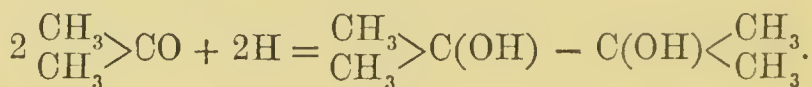
6. **Preparation of Isopropyl Iodide** $(CH_3 \cdot CHI \cdot CH_3)$.— Isopropyl iodide may be obtained from the alcohol by
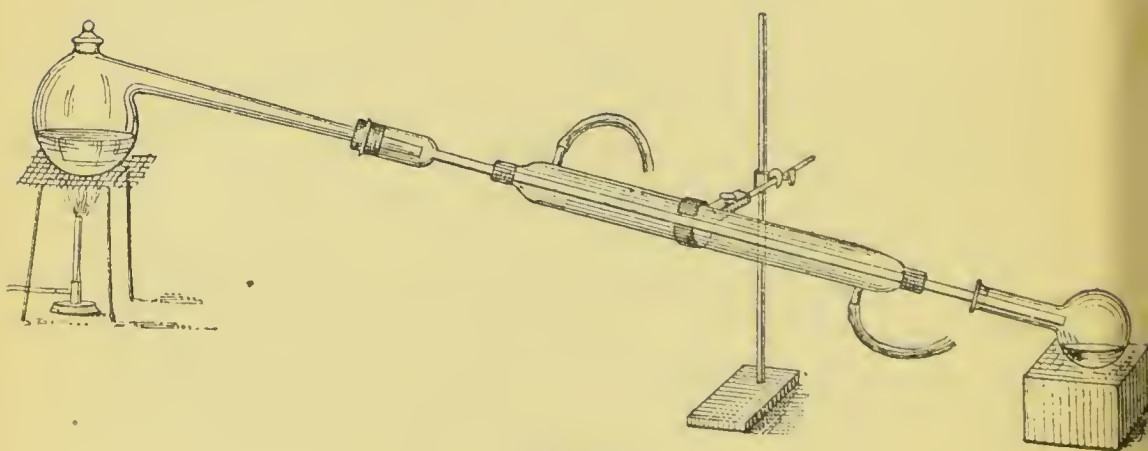
Fig. 50.

means of phosphorus and iodine ; it is, however, more conveniently produced from glycerine. In a retort of suitable size, provided with a condenser as shown in fig. 50, place 30 grams of iodine and 20 grams of glycerine (of sp. gr. 1·25), which has been diluted with 16 grams of water. Now add gradually in small portions at a time 5·5 grams

of yellow phosphorus. (The addition of phosphorus must be made with care since there is already iodine in the retort.)   The retort is then carefully heated, the contents being distilled as long as an oily liquid comes over.   Return the distillate to the retort and distil it over again.   The liquid so obtained has next to be washed with dilute sodium carbonate solution and then with water in a separating funnel ; finally it is separated from the water. dried over calcium chloride and rectified from a distilling flask.   Colourless liquid, boiling-point $89 \cdot 5°$.   Specific gravity $1 \cdot 7109$ at $15°$ (Linnemann).

In this preparation the iodine and phosphorus form phosphorus iodide which reacts on the glycerine, forming, not propenyl triodide $C_3H_5I_3$, but allyl iodide, C_3H_5I :

$$C_3H_5(OH)_2 + PI_3 = H_3PO_3 + I_2 + C_3H_5I.$$

The iodine is not obtained in the free state, but as hydrogen iodide under the influence of the water and phosphorus present.   This, then, serves to reduce the allyl iodide to isopropyl iodide :

$$\begin{array}{ccc} CH_2 & & CH_3 \\ \parallel & & \mid \\ CH & + \ 2\ HI\ = & CHI\ +\ I_2 \\ \mid & & \mid \\ CH_2I & & CH_3. \end{array}$$
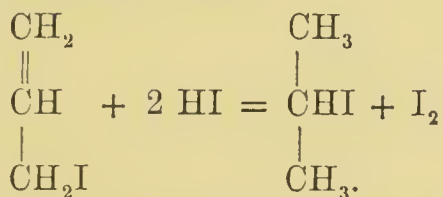
The iodine again unites with the phosphorus which has been added in considerable excess.

Recognition of Primary, Secondary, and Tertiary Alcohols. —The alcohols of the fatty series behave differently upon oxidation according to whether they are of primary, secondary, or tertiary constitution.   A primary alcohol first yields an aldehyde, then an acid, both compounds containing in their molecules as many atoms of carbon as the original

alcohol. The changes are rendered evident by the following scheme :

$$C_nH_{2n+1}\ CH_2OH \rightarrow C_nH_{2n+1}CHO \rightarrow C_nH_{2n+1}COOH.$$
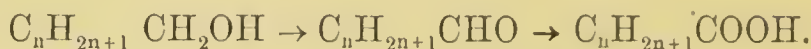
Secondary alcohols when oxidised first give a ketone with the same number of atoms per molecule as the alcohol ; further oxidation breaks up the molecule, a mixture of acids being produced.

$$\left.\begin{matrix}C_nH_{2n+1}\\C_mH_{2m+1}\end{matrix}\right\rangle CH(OH) \rightarrow \left.\begin{matrix}C_nH_{2n+1}\\C_mH_{2m+1}\end{matrix}\right\rangle CO \rightarrow \begin{matrix}C_nH_{2n}O_2\\C_{m+1}H_{2m+2}O_2.\end{matrix}$$
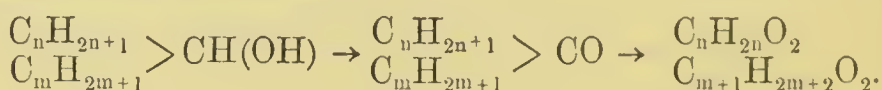
Tertiary alcohols when oxidised break up without giving any intermediate compound having the same number of carbon atoms per molecule.

A far simpler method of finding out whether an alcohol is primary, secondary, or tertiary was devised some years back by Victor Meyer, the first step being the conversion of the alcohol by iodine and phosphorus into the corresponding iodide, and then acting on the latter compound with silver nitrite. In this way a nitroparaffin is obtained, together with a certain amount of the isomeric nitrite according to the equation :

$$Alk{\cdot}I + AgNO_2 = Alk{\cdot}NO_2 + AgI.$$

The nitroparaffin so obtained reacts with nitrous acid if it be primary or secondary ; a tertiary nitroparaffin gives, however, no reaction. Nitroethane under these circumstances is converted into a nitrolic acid,

$$CH_3 \cdot CH_2 \cdot NO_2 + HNO_2 = CH_3 \cdot C{\Large\langle}\begin{matrix}^{\nearrow}NOH\\[2pt]_{\searrow}NO_2\end{matrix} + H_2,$$
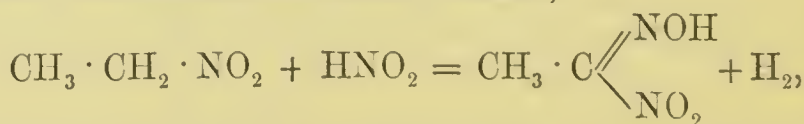
soluble in alkalies with a reddish shade. Iso-nitropropane, however, gives a pseudonitrol with nitrous acid ; the com-

pound is insoluble in alkalies, but dissolves in organic solvents with a blue colour:

$$CH_3 \cdot CH(NO_2) \cdot CH_3 + HNO_2 = CH_3 \cdot C(NO)(NO_2) \cdot CH_3 \\ + H_2O.$$
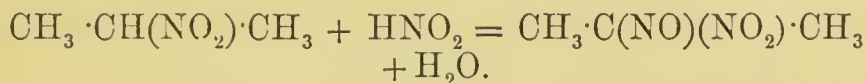
Tertiary nitrobutane, $C(CH_3)_3NO_2$, gives no reaction with nitrous acid.

7. **Preparation of Nitroethane** ($C_2H_5 \cdot NO_2$).—Dissolve 25 grams of silver nitrate in about its own weight of warm water (say at about 40°–50°) and add to this solution 16 grams of potassium nitrite, also dissolved in about its own weight of warm water. Stir well, allow to cool, and filter off the silver nitrite which is thus obtained as a white crystalline powder with the aid of the pump. Wash once or twice with cold water, spread on a piece of tile, and dry in a desiccator in the dark. Weigh out 20 grams of the dry silver nitrite thus prepared into a flask of about 100 c.cm. capacity; fit this with a cork through which a dropping funnel and a reflux condenser pass, as shown in fig. 51.
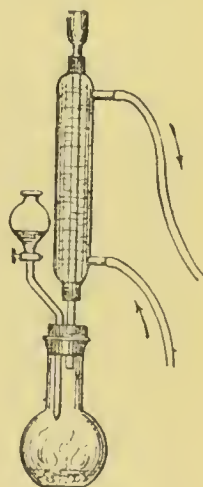
Fig. 51.

Place 16 grams of ethyl iodide in the dropping funnel, and run it on to the silver nitrite at such a rate that the liquid boils, but not too violently. When all the ethyl iodide has been added boil the contents of the flask for two hours on the water-bath, then reverse the condenser and distil off all the liquid which will come over below 100°. This first fraction of the distillate should be received in a small bottle, which must be tightly corked when removed from the end of the condenser, since the liquid it contains

is volatile.   Now substitute a fresh receiving vessel, and in place of the water-bath use an oil or sulphuric acid bath, distilling as long as any liquid comes over. This second distillate consists chiefly of nitroethane, the liquid boiling below 100° consisting principally of ethyl nitrite and unacted-on ethyl iodide, whilst a mixture of silver nitrite and iodide is left behind in the flask.   This residue is finely powdered, returned to the flask, and again digested under reflux with that portion of the distillate which came over below 100°.   On again distilling, a further quantity of nitroethane is obtained, which is added to that obtained by the first distillation.   The united quantities are allowed to stand overnight in a bottle containing 1 gram of silver nitrite and tightly corked.   On submitting the resulting liquid to distillation, nitroethane is obtained as a colourless liquid, boiling at 113°–114°.   Yield about 3 grams.

In a test-tube place 2 c.cm. absolute alcohol.   Dissolve in this a small piece of sodium.   On adding a drop of nitroethane to this solution, a colourless precipitate of sodium nitroethane, $C_2H_4NaNO_2$, is thrown down.   Add 3 or 4 c.cm. water, then a drop or two of ferric chloride; a blood red colour is produced.[1]

To try the nitrolic acid reaction, dissolve a few drops of

[1] The formula of the salts of the nitroparaffins has been a matter of discussion.   At first it was supposed that sodium nitroethane had the constitution $CH_3 \cdot CHNa \cdot NO_2$.   J. U. Nef considered the salt to be $CH_3 \cdot CH : N \overset{/\!\!/ O}{-} ONa$.   During the passage of this work through the press interesting papers by Hantzsch and Schultze have appeared in the *Berichte*, 1896, **29**, 699 and 2251.   In these it is shown that when phenylnitromethane, $C_6H_5 \cdot CH_2 \cdot NO_2$, is dissolved in alkali, and then separated by addition of acid, that an unstable isomeric form is precipitated which melts at 84°.   This, however, passes on standing into the original oily phenylnitromethane of the formula $C_6H_5 \cdot CH_2 \cdot NO_2$.   On

nitroethane in a little weak caustic soda, then add a
solution of potassium nitrite, and acidify so that nitrous
fumes are evolved.   On again rendering alkaline a reddish
brown solution will be obtained.

   8. **Preparation of Isonitropropane** $(CH_3 \cdot CH(NO_2) \cdot CH_3)$.
—Prepare a specimen of isonitropropane, proceeding in the
same way as described for nitroethane but using 20 grams
of silver nitrite and $17\frac{1}{2}$ grams of isopropyl iodide.   Iso-
nitropropane is a colourless liquid, slightly heavier th $\imath$ n
water and boiling at $115°–118°$.   Like nitroethane, it forms
a sodium compound, $C_3H_6NaNO_2$.

   Prepare a small quantity of propylpseudonitrol by dis-
solving a few drops of the nitro-compound in dilute caustic
potash solution, adding a solution of potassium nitrite and
then acidifying by dilute sulphuric acid, cooling the test-
tube and its contents meanwhile by tap-water.   The liquid
takes on a blue shade, then the propylpseudonitrol separates
out in the solid condition, insoluble in alkaline, neutral, or
acid solutions.   It dissolves, however, in alcohol or chloroform
with a blue colour.

Section III.—Monobasic Acids

   A large number of fatty acids are found in nature as
esters of the triacid alcohol glycerine (*e.g.* palmitic, stearic,
oleïc acids), others are formed in various fermentative pro-
cesses (*e.g.* acetic, propionic, butyric acids).   They are
consequently but rarely prepared by synthetical methods

account of the acid properties of the new isomer, Hantzsch ascribes to
it the formula $C_6H_5 \cdot CH - N \cdot OH$, and writes the sodium salt as;
$$\overset{}{\underset{O}{\diagdown\diagup}}$$

$$C_6H_5 \cdot CH - N \cdot ONa,$$
$$\overset{}{\underset{O}{\diagdown\diagup}}$$
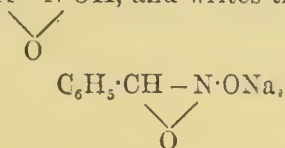
in practice, although they may be obtained by hydrolysis of alkyl cyanides, which in turn may be prepared from alkyl halogen compounds and potassium cyanide. The hydrolysis of such a cyanide may be effected by heating either with acids or alkalies, the change being represented by the following general equations :

$$Alk \cdot CN + HCl + 2H_2O = Alk \cdot COOH + NH_4Cl.$$

$$Alk \cdot CN + KOH + H_2O = Alk \cdot COOK + NH_3.$$
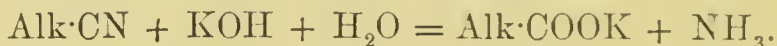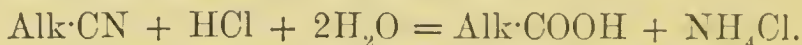
We shall study an example of such a reaction when we come to the dibasic acids of the general type, $C_nH_{2n}(COOH)_2$.

As previously mentioned, the primary alcohols may be converted first into aldehydes and then into acids on oxidation.

From the monobasic acids, not only salts, but also a large number of other derivatives may be obtained. By the action of the halogen derivatives of phosphorus, they are converted into acid halides, e.g. acetic acid and phosphorus trichloride yield acetyl chloride :

$$3CH_3COOH + PCl_3 = 3CH_3 \cdot COCl + H_3PO_3.$$
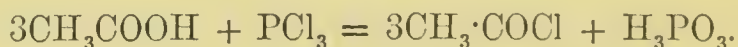
When an acid chloride acts on a salt of the acid, the anhydride is obtained :

$$CH_3COCl + CH_3COONa = (CH_3CO)_2O + NaCl.$$
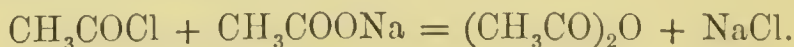
The amides of the acids are obtained in a variety of ways. When ammonia acts on an acid chloride, an acid amide and ammonium chloride are produced:

$$CH_3COCl + 2NH_3 = CH_3CONH_2 + NH_4Cl.$$
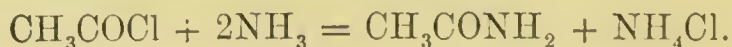
An ethyl ester and ammonia give an amide and ethyl alcohol :

$$CH_3 \cdot COOC_2H_5 + NH_3 = CH_3 \cdot CONH_2 + C_2H_5OH.$$
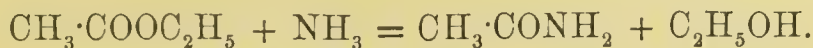
Ammonium salts lose water on heating :

$$CH_3COONH_4 = CH_3 \cdot CONH_2 + H_2O.$$

Further dehydration (phosphorus pentoxide is used) gives the corresponding nitrile :

$$CH_3CONH_2 = CH_3 \cdot CN + H_2O.$$
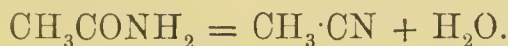
Conversely, the nitriles may be made to take up water with formation of amides :

$$CH_3CN + H_2O = CH_3 \cdot CONH_2.$$
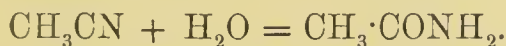
The esters of the acids may be prepared in a variety of ways, amongst which may be mentioned the action of alkyl halides on the salts of the acids, and the action of the alcohols on the acids under the influence of sulphuric or hydrochloric acid ; *e.g.*

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3 \cdot COOC_2H_5 + H_2O.$$

9. **Preparation of Acetyl Chloride** ($CH_3 \cdot COCl$).—This compound is best prepared by distilling a mixture of phosphorus trichloride and glacial acetic acid, the reaction following the equation :

$$3CH_3COOH + PCl_3 = 3CH_3 \cdot COCl + H_3PO_3.$$
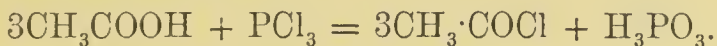
The apparatus required for the purpose is shown in fig. 52. In a tubulated retort of 200 to 300 c.cm. capacity are placed 35 grams of glacial acetic acid, whilst the stoppered funnel which passes through the tubulus contains 30 grams of phosphorus trichloride. Do not allow greater access of air to the phosphorus trichloride than you can avoid, the compound reacts very readily with water forming phosphorous and hydrochloric acids. The
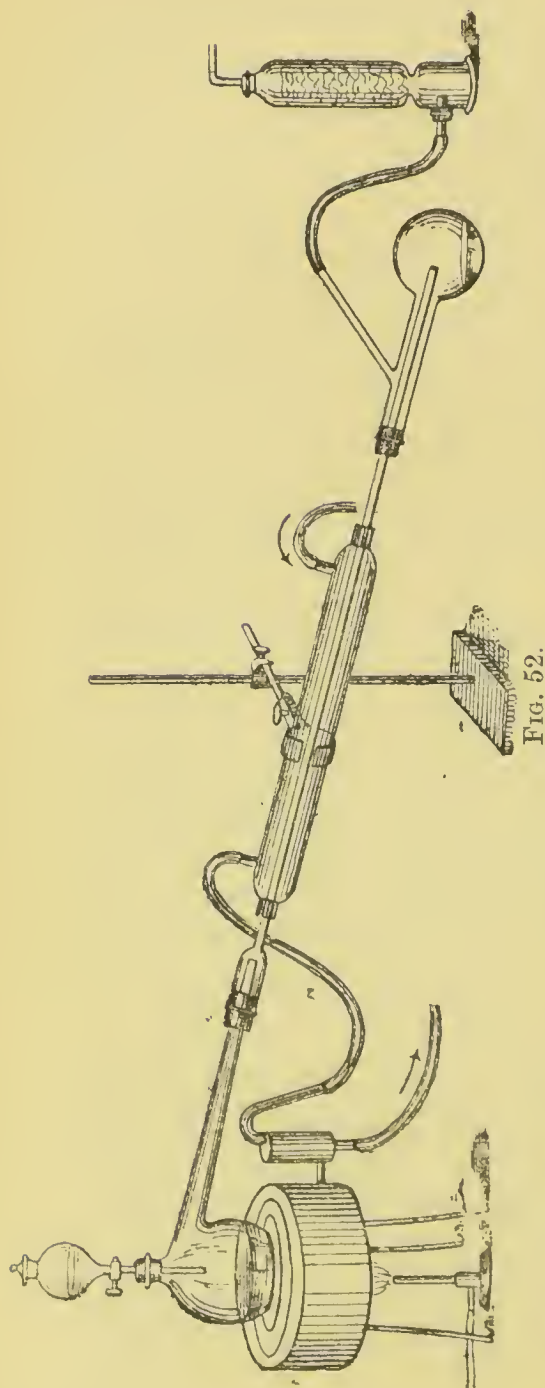
FIG. 52.

retort stands on a water-bath (cold) and is connected with a Liebig's condenser; the water used to cool the condenser can be employed to feed the water-bath by the arrangement of tubing shown. The further end of the condenser passes through a sound cork into a distilling flask, the side tube of which is in turn connected with a tower containing quicklime. All the joints should be perfectly tight, since acetyl chloride is extremely irritating both to eyes and throat; the lime tower is to hold back any of the vapour which may pass beyond the distilling flask. The phosphorus trichloride is run into the acetic acid, reaction takes place almost immediately, the mixture in the retort becoming slightly warmed, whilst hydrochloric acid gas is also evolved (probably owing to the pre-

sence of a little water in the acetic acid).   When all the phosphorus trichloride has been poured in, the liquid, which has meanwhile separated into two layers, is distilled by raising the water in the water-bath to boiling ; in this way the upper layer of acetyl chloride is driven over, whilst the lower somewhat viscous layer consisting of phosphorous acid and excess of acetic acid remains in the retort.

The distilling flask is now disconnected, provided with a thermometer and condenser, and the acetyl chloride distilled over by means of a naked flame.   Acetyl chloride is a sharp-smelling, colourless, mobile liquid which fumes on exposure to the air,[1] boils at 55° and has a specific gravity of $1 \cdot 1305$ at 0° C.   Yield, 30–35 grams.

Pour a drop or two of the acetyl chloride into 2 c.cm. of water contained in a test-tube. The acetyl chloride dissolves in the water, forming acetic and hydrochloric acids :

$$CH_3COCl + H_2O = CH_3COOH + HCl.$$
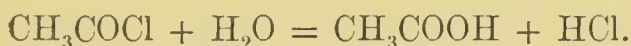
Similarly, pour two drops into 1 c.cm. alcohol in a test-tube : warm gently, the fruity smell of ethyl acetate will be noticed :

$$CH_3COCl + C_2H_5OH = CH_3COOH + HCl.$$
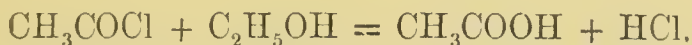
This furnishes an additional, and in some cases very useful, way by which to prepare esters.

10. **Preparation of Acetic Anhydride** $[(CH_3 \cdot CO)_2O].$—As previously mentioned, acetic anhydride can be prepared by the action of acetyl chloride on sodium acetate. The latter salt must be, however, fully dehydrated, otherwise

---

[1] The distillate must be preserved in well-stoppered vessels or sealed tubes.

acetic acid will be obtained. Weigh out 60 grams of crystal-
lised sodium acetate $(CH_3COONa,3H_2O)$ into a shallow
iron dish and warm this by means of a Bunsen burner.

The dehydration is carried out as described previously
by the preparation of methane (see p. 104); finely powder
the dehydrated salt, and if it is not required for imme-
diate use transfer it to well-stoppered bottles. From the
quantity of crystallised sodium acetate taken, about 35
grams of the dehydrated salt should be obtained. Fit up
apparatus similar to that represented in fig. 52 for the
preparation of acetyl chloride, but put in the retort 33
grams of powdered sodium acetate and in the stoppered
funnel 30 grams of acetyl chloride. Also arrange the re-
tort and water-bath (cold) in such a way that the retort can
be cooled by plunging it into water. Now allow the
acetyl chloride to flow in gradually on to the powdered
sodium acetate, cooling the retort from the outside with
cold water. The reaction takes place principally during
this operation ; stir the contents of the retort thoroughly
together with a stout glass rod, and complete the reaction
by heating the retort to 100° on the water-bath ; after
twenty minutes at this temperature the water-bath can be
removed, the outside of the retort carefully wiped, and an
oil-bath substituted for the water-bath. On raising the
temperature of the oil-bath, the acetic anhydride will distil
over into the boiling-point flask, from which it can after-
wards be rectified. Colourless liquid, boiling point 138°.
Yield, about 30 grams.

Pour a few drops into water; it will be found that the
smell of acetic anhydride does not immediately give place
to that of acetic acid, although the latter is somewhat
rapidly produced. The solution should give no precipitate
with silver nitrate solution. On warming a few drops of

acetic anhydride with alcohol, the smell of ethyl acetate will be noticeable.

11. **Preparation of Acetamide.** $(CH_3 \cdot CONH_2)$—It has previously been stated, on pp. 128, 129, that acetamide may be prepared in a variety of ways, such as the action of ammonia on acetic anhydride or chloride, or by the interaction of ammonia and ethyl acetate. In addition to these methods, ammonium acetate may be deprived of a molecule of water by distillation; this process will now be described.

Weigh out 60 grams of glacial acetic acid into a flask of about 300 or 400 c.cm. capacity, and add solid ammonium carbonate in small pieces at a time. The addition of the latter salt should be cautiously made, and continued until the liquid shows a neutral or slightly alkaline reaction. Pour the solution so obtained whilst it is still hot into a distilling flask provided with a thermometer; the side tube should not be connected with a condenser but passed through a cork into a tube of about 15 mm. internal diameter and about 1 metre long. Now heat the contents of the retort slowly; much ammonia and water come over at first, these products being succeeded by acetic acid, the thermometer remaining for some time in the neighbourhood of 155°. Above 160° acetamide will pass over and condense in the cooling tube to a crystalline mass; when the distillation is finished either scrape the mass of acetamide out of the tube by a long glass rod or melt it out. Submit the product so obtained to a second distillation from a boiling-point flask, using no condenser, but, as in the previous case, a cooling tube, which should be somewhat shorter (about 50 cm.), and collect all that comes over above 180° as acetamide. The acid distillate which came over in the first distillation, before the acetamide, should be again neutralised with ammonium carbonate

and once more distilled. In this way 17 or 18 grams of acetamide will be obtained in the form of a white crystalline mass, having a very characteristic smell resembling that of the excrement of mice. Acetamide may be obtained quite pure and odourless by recrystallisation from ether;
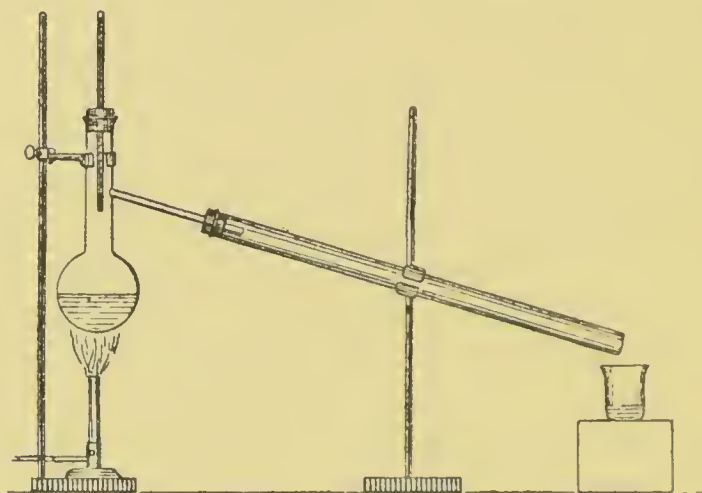
FIG. 53.

it then forms long colourless needles which melt at 82° and boil at 222°.

Acetamide combines with acids, forming unstable salts such as CH_3CONH_2, HCl and $CH_3 \cdot CONH_2$, HNO_3; these have a strong acid reaction. On the other hand, one of the hydrogen atoms of acetamide may be replaced by metals; silver acetamide, $CH_3CONHAg$, and mercury acetamide, $(CH_3CONH)_2Hg$, are known. Whether the latter compounds are to be regarded as derived from acetamide by replacement of hydrogen of the amido group by metal appears doubtful, since Tafel and Enoch obtained ethyl imidobenzoate and not the isomeric benzoethylamide by the action of ethyl iodide on the silver derivative of benzamide :

$$C_6H_5 \cdot C\!\!\begin{array}{c} \nearrow NH \\ \searrow OAg \end{array} + C_2H_5I = AgI + C_6H_5 \cdot C\!\!\begin{array}{c} \nearrow NH \\ \searrow OC_2H_5 \end{array}$$

$$(\text{not } C_6H_5 \cdot C\!\!\begin{array}{c} \nearrow O \\ \searrow NHC_2H_5 \end{array}).$$
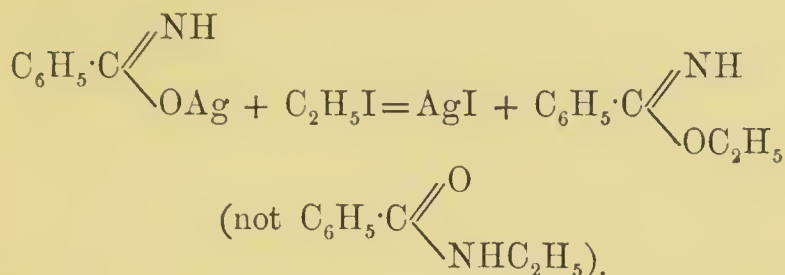
The acid amides appear to be capable of reacting tautomerically either as

$$R \cdot C\!\!\begin{array}{c} \nearrow O \\ \searrow NH_2 \end{array} \quad \text{or} \quad R \cdot C\!\!\begin{array}{c} \nwarrow OH \\ \searrow NH. \end{array}$$
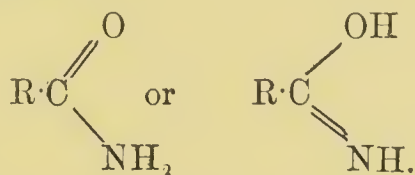
12. **Preparation of Acetonitrile** (CH_3CN).—Strong dehydrating agents, such as phosphorus pentoxide or pentasulphide, are necessary to remove a molecule of water from acetamide and effect its conversion into acetonitrile. Into a small dry tubulated retort connected with a condenser introduce 25 grams of phosphorus pentoxide and then 10 grams of dry powdered acetamide. Mix the substances thoroughly by means of a glass rod, and cover the mixture with a layer of 10 grams of phosphorus pentoxide. Heat the retort with a rather large flame; acetonitrile will distil over and should be collected in a small distilling flask. On submitting the distillate to fractionation, acetonitrile passes over as a colourless liquid boiling at 81·5°.

The nitriles of the acids may be hydrolysed to the corresponding acid and ammonia, the reaction taking place more easily in presence of an acid or an alkali. In the former case the free acid and the ammonium salt of the acid used to effect hydrolysis are produced, in the

latter case a salt of the organic acid and free ammonia, the reactions in the case of acetonitrile and hydrochloric acid and caustic potash respectively being expressed by the equations :

$$CH_3 \cdot CN + 2H_2O + HCl = CH_3 \cdot COOH + NH_4Cl.$$
$$CH_3 \cdot CN + H_2O + KOH = CH_3 \cdot COOK + NH_3.$$
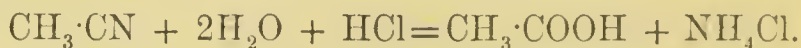
The first reaction can be quantitatively followed, the following experiment being easily performed :—Weigh out accurately and seal off in a thin glass bulb ·4 to ·5 gram of the acetonitrile, and, having a stout walled glass tube, sealed and rounded off at one end, cleaned and ready, prepare a hydrochloric acid of roughly 20 per cent. strength by mixing 10 c.cm. of the pure fuming acid with an equal volume of water. The strength of the solution must be found exactly by titration. Drop into the sealed tube 5 c.cm. of the acid so prepared by means of a pipette, then introduce the thin walled bulb and its contents and seal off the end of the tube in the manner described on page 58. By shaking the sealed tube, the bulb contained in it may be broken and its contents mixed with the hydrochloric acid : then heat for three hours to a temperature of 150°. After cooling, open the tube and rinse the whole contents into a measuring flask of 250 c.cm. capacity, remembering not only to rinse out thoroughly the long end of the tube, but also the short end which was cut off when the tube was opened. Make the volume up to 250 c.cm. with distilled water, take out 25 c.cm. of the solution with a pipette, and titrate with decinormal sodium hydroxide solution, using litmus or phenolphthalein as an indicator. (The organic acids give uncertain results with methyl orange.) Repeat the titration two or three times and take the mean result, which should correspond with

what would have been obtained if 5 c.cm. of the original 20 per cent. hydrochloric acid had been taken, made up to 250 c.cm., and then 25 c.cm. had been titrated ; since, although hydrochloric acid has been used in the formation of ammonium chloride, an equivalent amount of acetic acid has been liberated.

To determine the ammonia take a further 25 c.cm. of the solution, add to it double the volume of the decinormal soda necessary to effect neutralisation, and boil until the whole of the ammonia is expelled. This will necessitate vigorous boiling of the solution ; care must be taken that none of the liquid splashes out. By a back titration of the soda not employed in expelling the ammonia from the ammonium chloride with decinormal acid, the amount of ammonia may be determined, and a simple calculation will give the total amount of ammonia produced when the acetonitrile used was hydrolysed.

Section IV.—Dibasic Acids

The simplest dibasic carbon acid is carbonic acid, $CO(OH)_2$, which, though not occurring in the free state, is known not only in the form of salts and esters but also as the acid chloride, $COCl_2$; the amide (urea), $CO(NH_2)_2$, and the amidine (guanidine), $C(NH)(NH_2)_2$. We now proceed to the preparation of these substances.

13. **Preparation of Carbonyl Chloride** ($COCl_2$).— Carbonyl chloride, which may be obtained by the direct union of carbon monoxide and chlorine in sunlight, is most readily prepared by the action of fuming sulphuric acid (80 per cent. sulphur trioxide) on carbon tetra-chloride, the reaction following the course expressed by the equation :

$$CCl_4 + 2SO_3 = COCl_2 + S_2O_5Cl_2.$$
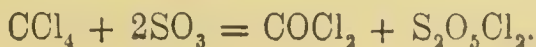
The pyrosulphuryl chloride so formed reacts further with the sulphuric acid of the fuming acid to produce sulphur trioxide and chlorsulphonic acid, so that the residue of the preparation forms an energetic and useful sulphonating agent and should be preserved for this purpose. The carbonyl chloride can either be condensed to the liquid form by means of cold (the boiling-point of the compound is 8°), or it can be absorbed by dry toluene and kept as a 20 per cent. solution for further use. The preparation described here is based on the results given by H. Erdmann (*Ber.* 1893, **26**, 1990.)

Fifty grams (*i.e.* nearly 30 c.cm.) of carbon tetra-
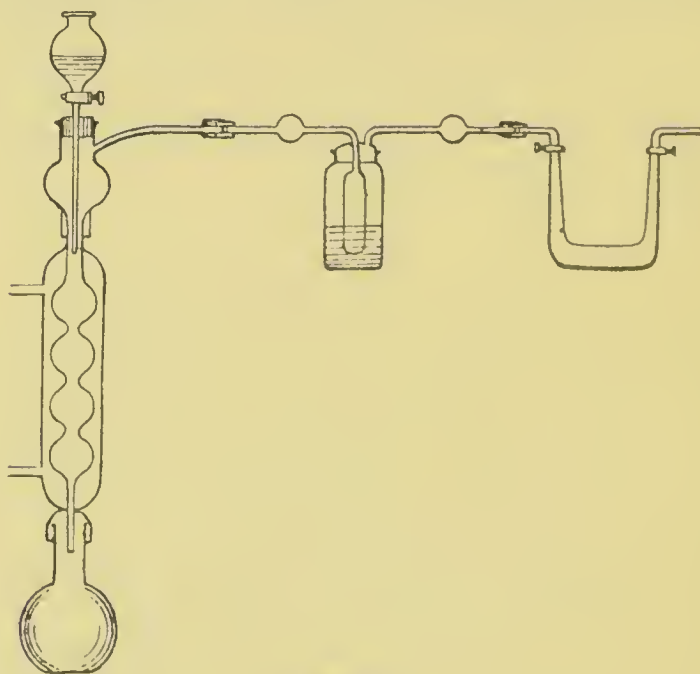
Fig. 54.

chloride are heated in a flask of 100–120 c.cm. capacity to boiling by means of a water-bath, the flask being connected with a reflux condenser having four bulbs blown on the inner tube as shown in fig. 54. At the top of the adaptor,

with side tube fitted to the top of the condenser, is a dropping funnel from which 36 c.cm. of fuming sulphuric acid (with 80 per cent. sulphur trioxide) are gradually dropped into the boiling carbon tetrachloride ; the end of the funnel being, however, at such a height that each drop of the acid has to come very thoroughly in contact with the vapours ascending from the flask as it makes its way to the flask.   By regulating the rate at which the fuming acid drops in, a regular stream of carbonyl chloride may be obtained, which passes by the side tube into a glass washing bottle (no corks or india-rubber stoppers can be used) containing strong sulphuric acid to hold back the vapours of sulphur trioxide and pyrosulphuryl chloride, and then into a Hofmann's receiver in which the gas is condensed by means of a freezing mixture.   The washing bottle containing the sulphuric acid should stand in a beaker of cold water, as it very readily becomes warm ; the joints between the tubes may be made by means of good india-rubber connection tubing, but in all cases the glass must abut on glass.   As soon as all the fuming sulphuric acid has been added, and the evolution of gas ceases, the contents of the flask are raised to boiling by the naked flame so as to drive out all the dissolved carbonyl chloride, which is condensed with the rest of the gas in the Hofmann's receiver.   This latter should be weighed before and after the experiment ; it will be found that about 28 or 29 grams of crude carbonyl chloride are produced.   To purify the product and prepare the toluene solution, connect one end of the Hofmann's receiver to a wash bottle containing sulphuric acid, the other tube of which leads into an absorption flask containing four parts of dry toluene [1] for every part of

---

[1] The toluene may be dried first over calcium chloride, then over slices of sodium and distilled.

carbonyl chloride contained in the receiver. On turning on the glass stop-cock of the receiver and warming the latter by the hand, the carbonyl chloride will be volatilised, washed by the sulphuric acid, and dissolved by the toluene. The toluene solution must be kept in a closely-stoppered bottle.

The residue of sulphur trioxide and chlorsulphonic acid in the round-bottomed flask used in the preparation should be distilled, the distillate being preserved from contact with the air and kept for sulphonating purposes.

14. **Preparation of Carbamide (Urea)** $(CO(NH_2)_2)$.—Urea is prepared by the action of heat upon ammonium cyanate, which thereby undergoes an isomeric change, being transformed into carbamide according to the equation :

$$NH_4 \cdot CNO = CO(NH_2)_2.$$

In this preparation it is not necessary to employ pure dry potassium cyanate ; a solution of this salt can be obtained by extracting the mass formed on heating a mixture of yellow prussiate of potash and potassium dichromate with water, then adding ammonium sulphate to this solution and evaporating to dryness, whereby not only is the formation of potassium sulphate and ammonium cyanate effected, but the latter is also isomerised.

Heat 75 grams of the ordinary crystallised potassium ferrocyanide $(K_4Fe(CN)_6 \cdot 3H_2O)$ in a porcelain basin over a flame until all the water of crystallisation is expelled ; the mass must be stirred repeatedly with a glass rod during this operation, and the heating should not be stopped until on breaking up the crystals of the salt no yellow nucleus of hydrated salt is to be observed. Then powder the mass finely, spread it out in a thin layer in the porcelain dish, and heat for a further two hours to 150°. Further fuse

45 grams of potassium dichromate so that the latter salt may also be fully dehydrated, then powder the salt finely.

Mix intimately together 50 grams of the dried potassium ferrocyanide with 38 grams of the fused potassium dichromate, and throw the mixture in small quantities at a time into a large iron dish heated in such a way that each portion as thrown in is raised to incandescence and forms a black mass, but on no account fuses.   In this way a mass containing the oxides of iron, chromium, and potassium is obtained, the reaction being expressed by the equation :

$$K_4Fe(CN)_6 + 2K_2Cr_2O_7 = 6KCNO + 2Cr_2O_3 + FeO + K_2O.$$
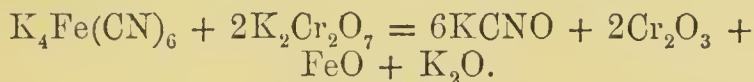
Extract the potassium cyanate from the mass with three successive portions of cold water, each of 200 c.cm., unite the three filtrates in a suitably-sized evaporating basin, add 37 grams of ammonium sulphate, and evaporate to dryness on the water-bath.   Extract the residue with alcohol, filter from undissolved potassium sulphate, and evaporate to dryness again.   (This is best done by distilling off the alcohol by means of a water-bath.)   Recrystallise the residue of urea from 200 c.cm. of amyl alcohol.   The mother liquor from this recrystallisation still contains urea ; evaporate the excess of solvent, add water, then nitric acid, and isolate the remainder of the urea in the form of its nitrate ; this salt, being but sparingly soluble, readily crystallises out.

15. **Preparation of Guanidine Thiocyanate** (CN_3H_5, HCNS).—By heating ammonium thiocyanate (a far more stable compound than the corresponding cyanate), thiocarbamide may be obtained according to a reaction similar

to that which takes place during the intramolecular change of ammonium cyanate :

$$NH_4CNS = CS(NH_2)_2.$$

At a high temperature the reaction easily goes further, the thiourea reacting with more of the ammonium salt, sulphuretted hydrogen being split off, and the thiocyanate of guanidine being formed :

$$CS(NH_2)_2 + NH_4CNS = H_2S + C(NH)(NH_2)_2HCNS.$$
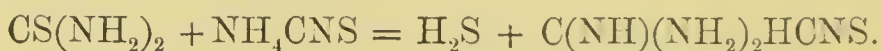
Dry commercial ammonium thiocyanate thoroughly, heat an oil-bath to 190°–200°, weigh 200 grams of the dried ammonium thiocyanate into a flask of 500 c.cm. capacity, and heat this flask in the oil-bath for twenty hours.   In this way the melt will be kept at a temperature of 180°–190°.   The reaction must in any case be carried out in a draught cupboard, and it is as well to lead the gases which escape during the reaction into a washing bottle containing water, to absorb and condense the greater part of the ammonia and sulphides of hydrogen and carbon which escape during the process.   About 140 grams of crude guanidine thiocyanate will be left in the flask when the heating is finished ; the mass is crystalline, but has a greenish colour, although it is sufficiently pure for many purposes.   To purify the substance, finely powder the melt and dissolve in one-fifth of its weight of boiling water. The salt which crystallises on cooling is to be filtered off by the aid of the pump, and dried on porous earthenware. Large leaflets, melting point 118°.

From the guanidine thiocyanate so obtained the other salts of the base may be obtained.   The carbonate, $(CN_3H_5)_2$ H_2CO_3, can be obtained by double decomposition with potassium carbonate in hot concentrated solution ; the two

products, guanidine carbonate and potassium thiocyanate, may be separated by evaporating the solution to dryness, and extracting the latter compound by solution in hot methylated spirit, in which the guanidine salt is practically insoluble. For this preparation recrystallised guanidine thiocyanate should be used.

Some very interesting compounds have of late years been obtained from guanidine by Thiele and his pupils. The sulphocyanic acid may be expelled by dissolving the crude guanidine thiocyanate in concentrated sulphuric acid. If to the solution of guanidine sulphate so obtained, first fuming sulphuric acid and then fuming nitric acid be added in succession, and the liquid be poured into water, nitroguanidine is precipitated in the form of needles. This compound has the formula $C(NH)(NH_2)(NH \cdot NO_2)$, and may be reduced to a strongly basic compound, amidoguanidine, $C(NH)(NH_2)(NH \cdot NH_2)$, which, like other hydrazines, reacts easily with aldehydes and ketones. By the action of nitrous acid the amidoguanidine is converted into amidotetrazole :

$$NH_2 \cdot C\!\!\begin{cases} NH \cdot NH_2 \\ NH \end{cases} + HNO_2 = NH_2 \cdot C\!\!\begin{cases} NH \cdot N \\ \parallel \\ N \cdot N \end{cases} + 2H_2O.$$
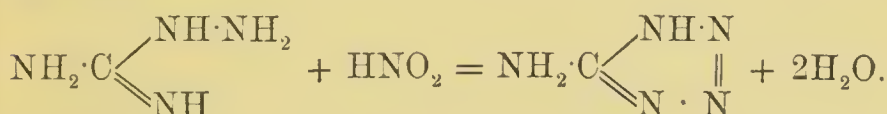
The resulting amido-compound is further acted on by nitrous acid giving diazo-compounds which react with phenols forming dyestuffs.

16. **Preparation of Malonic Acid** $(CH_2(COOH)_2)$.—Malonic acid may be prepared from chloracetic acid by first neutralising the acid group with potassium carbonate, then replacing the chlorine atom by a cyanogen group and finally hydrolysing the latter to a carboxyl group and ammonia :

$$CH_2 {\Large\langle}^{Cl}_{COOK} + KCN = KCl + CH_2 {\Large\langle}^{CN}_{COOK} \cdot$$

$$CH_2 {\Large\langle}^{CN}_{COOH} + HCl + 2H_2O = NH_4Cl + CH_2 {\Large\langle}^{COOH}_{COOH}$$
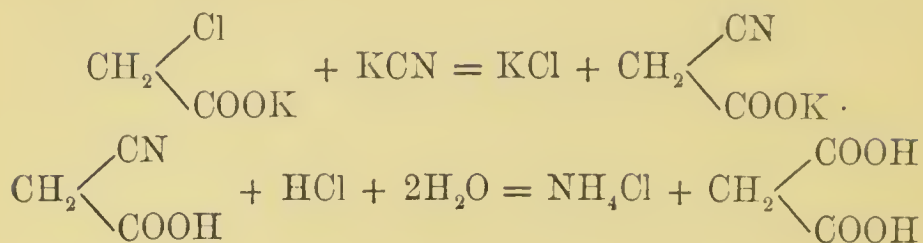
Dissolve 20 grams of chloracetic acid in 40 grams of water and neutralise the liquid by adding 15·2 grams of potassium carbonate. Then further add 15 grams of potassium cyanide of 98 per cent. strength [1] (draught cupboard), and warm the mixture on the water-bath. When the reaction between the potassium chloracetate and potassium cyanide is at an end, the appearance of boiling ceasing, add twice the volume of concentrated hydrochloric acid and saturate the liquid with hydrochloric acid gas. The gas for this purpose can be most readily generated by dropping concentrated sulphuric acid into concentrated hydrochloric acid contained in a roomy flask, and washing the gas evolved by passing it through strong sulphuric acid. When the liquid is fully saturated it will be found that potassium chloride and ammonium chloride have separated out, these two salts being but sparingly soluble in concentrated hydrochloric acid. Allow the salts to subside, pour off the liquid as completely as possible into an evaporating basin, wash the residual salts once with concentrated hydrochloric acid, decanting the washings into the basin, and evaporate to dryness on the water-bath. The malonic acid so obtained will be mixed with a small amount of the chlorides of potassium and ammonium, therefore extract the malonic acid from the dry residue with ether, distil off the ether

---

[1] If the potassium cyanide is weaker than this add a correspondingly greater weight.

with the aid of a water-bath, and recrystallise the residual malonic acid from a small quantity of water.   Malonic acid forms colourless leaflets melting at 132°.

17. **Preparation of Succinonitrile and Succinic Acid**,

$$\begin{array}{l} CH_2 \cdot COOH \\ | \\ CH_2 \cdot COOH \end{array}$$

.— When an alcoholic solution of ethylene dibromide and potassium cyanide are heated together on the water-bath, ethylene dicyanide (succinonitrile) and potassium bromide are produced.   The former substance may be isolated by fractional distillation *in vacuo* ; in this preparation we shall, however, hydrolyse the succinonitrile directly by boiling with potash without previously removing it from the alcohol in which it is dissolved.

The reactions involved may be expressed by the equations :

$$\begin{array}{l} CH_2Br \\ | \\ CH_2Br \end{array} + 2KCN = 2KBr + \begin{array}{l} CH_2 \cdot CN \\ | \\ CH_2 \cdot CN \end{array}$$

$$\begin{array}{l} CH_2CN \\ | \\ CH_2 \cdot CN \end{array} + 2KOH + 2H_2O = 2NH_3 + \begin{array}{l} CH_2 \cdot COOK \\ | \\ CH_2 \cdot COOK. \end{array}$$
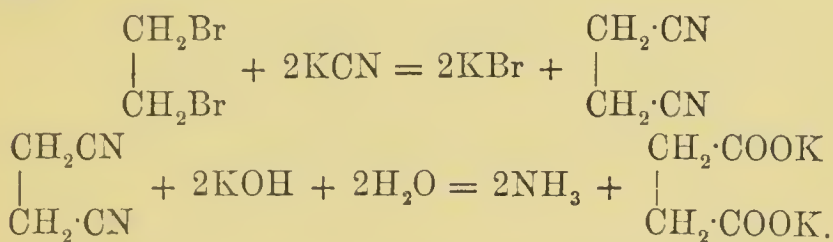
Add 20 grams of ethylene dibromide to 50 grams of absolute alcohol contained in a small flask provided with a reflux condenser.   To the mixture add further 17 grams of finely powdered 98 per cent. potassium cyanide, and boil the mixture under reflux on the water-bath for four hours.   Without in any way attempting to isolate the succinonitrile which is now contained in the solution, add 15 grams of stick caustic potash dissolved in an equal weight of water, and continue the boiling as long as ammonia is evolved.   Then allow to cool, add hydrochloric acid until the solution shows a strong acid reaction, filter if necessary,

L
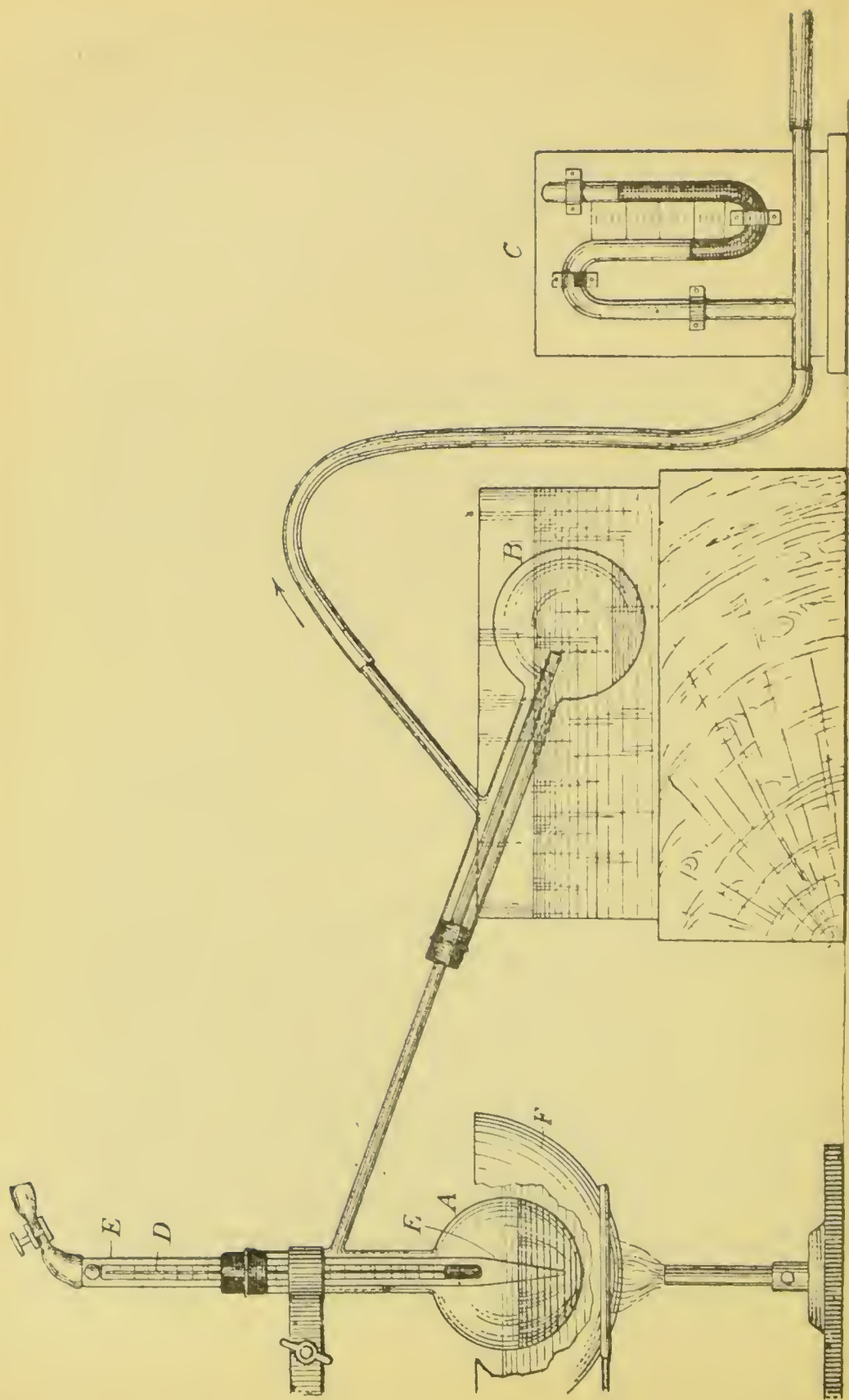
Fig. 5.

and evaporate to dryness on the water-bath. Powder the mass so obtained, boil with 50 c.cm. of methylated spirit, filter hot from the residue of potassium bromide and chloride, evaporate the filtrate to dryness on the water-bath, and recrystallise the residue from a small quantity of boiling water. Colourless monoclinic prisms, melting point 180°.

It has been stated above that, when it is desired to obtain the ethylene dicyanide in a pure state, it is necessary to distil the alcoholic solution *in vacuo*. This may be done in a fairly simple manner by joining two distilling flasks in the manner shown in fig. 55. The flask, A, containing the liquid to be distilled is connected by a thoroughly sound cork with the second flask, B. This acts as a receiver, and is immersed in a vessel containing cold water. The side tube of the flask B is connected by stout-walled india-rubber tubing to a filter pump, the shortened barometer, C, being introduced between the distilling apparatus and the pump, so as to obtain a register of the pressure during the distillation.

The heating of the flask A is effected by an oil-bath, F; part of this is shown broken away in the figure. The thermometer, D, is enclosed in a tube, E, drawn out at the lower end to a fine point; the upper end of E is connected with a short piece of india-rubber tubing closed with a pinch-cock. By this means a very slow current of air may be drawn through the apparatus during the process of distillation, and bumping thereby avoided.

It will be readily seen that, if desired, a condenser can easily be inserted between the distilling flask, A, and the receiving flask, B.

One disadvantage of the apparatus just described is that in changing the receiver to collect different fractions

of a distillate, air must first be admitted, and then the
vacuum again restored by the pump. This leads to much
waste of time. When several fractions have to be collected
it is better to use a Brühl's apparatus for receiving the
various fractions of the distillate.

This is represented in fig. 56. *A* is a vessel with
ground-glass cover; the tubulus of the cover is closed by
a good india-rubber stopper through which the handle, *B*, of
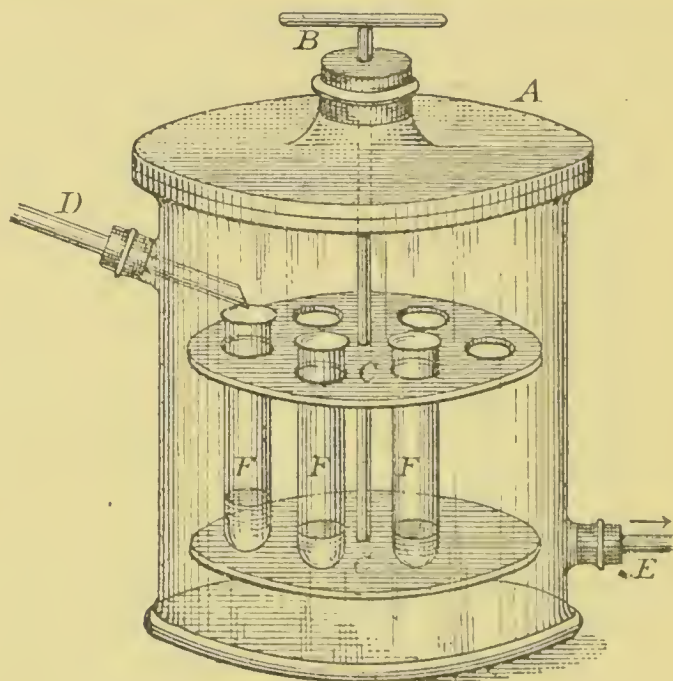
Fig. 56.

the carrier, *C*, passes. *D* represents the end of the con-
denser. *E* is a tube leading to a shortened barometer and
pump. By turning the handle *D*, various fractions may
be collected in the tubes *F*, *F*, supported by the carrier, *C*,
without either stopping the distillation or destroying the
vacuum,

18. **Preparation of Succinic Anhydride,** $\begin{array}{c} CH_2{\cdot}CO \\ | \qquad\quad{>}O. \\ CH_2{\cdot}CO \end{array}$

An internal anhydride of succinic acid can be obtained by simply submitting the acid to distillation. A readier way to remove a molecule of water is, however, to treat the acid with phosphorus pentachloride or oxychloride. Weigh into a flask of about 300 c.cm. capacity 100 grams of succinic acid which has been dried at 100°; pour on to this 65 grams of phosphorus oxychloride and heat to 120° under reflux in an oil-bath until no more hydrochloric acid gas is evolved. Then remove the condenser, fit the flask with a bent tube passing into a broad cooling tube, and subject the mixture to distillation over a naked flame. As soon as the distillate solidifies, immediately and completely as it cools, change the receiver and collect the succinic anhydride, which now comes over almost pure and colourless. Yield about 75 grams. Melting point 120°, boiling point 255°–257°.

In this reaction the phosphorus oxychloride acts as a dehydrating agent, being itself converted into phosphoric acid :

$$2C_2H_4(COOH)_2 + POCl_3 = HPO_3 + 3HCl$$
$$+ 2C_2H_4{<}{\begin{array}{c}CO\\CO\end{array}}{>}O.$$
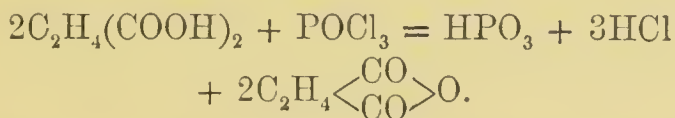
19. **Preparation of Citraconic Anhydride and Acid,**

$$\begin{array}{c} CH_3{\cdot}C{\cdot}CO \\ {\cdot}{\cdot} \qquad\quad {>}O \\ H{\cdot}C{\cdot}CO \end{array} \quad \text{and} \quad \begin{array}{c} CH_3{\cdot}C{\cdot}COOH \\ {\cdot}{\cdot} \\ H{\cdot}C{\cdot}COOH. \end{array}$$
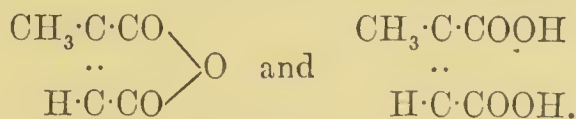
—When citric acid is heated, it first loses the elements of water passing into the unsaturated tribasic aconitic acid according to the equation:

$$
\begin{array}{l}
\text{CH}_2\text{·COOH} \\
| \\
\text{C(OH)·COOH} \\
| \\
\text{CH}_2\text{·COOH}
\end{array}
= \text{H}_2\text{O} +
\begin{array}{l}
\text{CH}_2\text{·COOH} \\
| \\
\text{C·COOH} \\
\| \\
\text{CH·COOH.}
\end{array}
$$
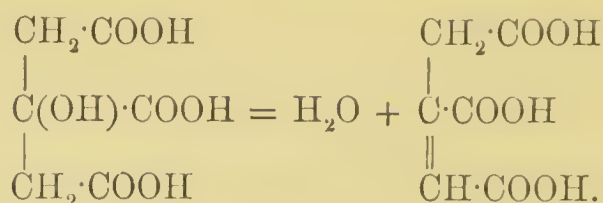
Further heating eliminates the carbon dioxide of the carboxyl group attached to CH_2; however, instead of obtaining the free acid $C_3H_4(COOH)_2$, the elements of water are lost by the two carboxyl groups and citraconic anhydride is formed according to the equation:

$$
\begin{array}{l}
\text{CH}_2\text{·COOH} \\
| \\
\text{C·COOH} \\
\| \\
\text{CH·COOH}
\end{array}
=
\left.
\begin{array}{l}
\text{CH}_3 \\
| \\
\text{C·CO} \\
\| \\
\text{CH·CO}
\end{array}
\right\rangle \text{O} + \text{H}_2\text{O} + \text{CO}_2.
$$
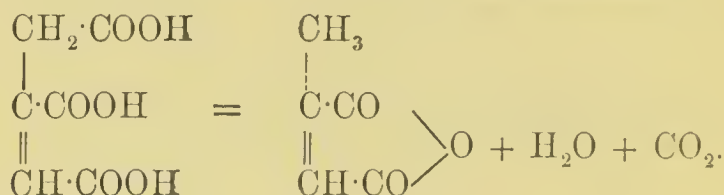
Generally speaking, dibasic acids in which the carboxyl groups are attached to adjacent doubly-linked carbon atoms readily lose water and form the corresponding anhydrides.

Place 100 grams of citric acid which has been thoroughly dried at 100° in a retort of at least 300 c.cm. capacity,[1] connect this with a condenser the end of which passes into a boiling-point flask, the tube of which is connected with tubing leading either into the draught or into a burning Bunsen burner. This precaution is taken as the gases evolved during the distillation are exceedingly irritating. Distil the contents of the retort as rapidly as possible by means of a large flame, taking care, of course, that none of the molten citric acid boils over into the condenser. Stop the distillation when the distillate takes on

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[1] It is better to use a non-tubulated retort for the purpose, as it is almost certain to perish in the distillation.

a dark brown colour ; the residue in the retort will swell up at the same time to a porous coaly mass.

The boiling-point flask which has been used as a receiver now contains water, citraconic acid, and citraconic anhydride; connect it with a condenser, insert a thermometer and subject the liquid to fractional distillation. At first water comes over, carrying, however, small quantities of citraconic anhydride with it ; the acid in the distilling flask is, however, completely decomposed by this treatment into water and the anhydride. As soon as all the water has been expelled, the thermometer will be seen to rise rapidly ; collect apart as citraconic anhydride all that distils between 210° and 220°. The citraconic anhydride forms a pale yellow oily liquid which solidifies in a freezing mixture and melts again at + 7° ; the boiling point is at 213°–214°. The aqueous first fraction can be allowed to evaporate slowly over sulphuric acid at the ordinary temperature in a crystallising dish ; colourless crystals of citraconic acid will in this way be obtained. Melting point 80°.

Citraconic acid easily passes into an isomeric compound known as mesaconic acid. The change may be brought about either by warming with dilute acids or by heating with water in sealed tubes to 180°. The new acid has the same constitution (as far as linkages are concerned) as the citraconic acid from which it is prepared ; it is not, however, capable of furnishing an anhydride of its own. When dehydrated by means of acetyl chloride, citraconic anhydride results. The isomerism of the two acids is explained by assigning to the two compounds a different arrangement of their atoms in space, as in the diagrams on p. 152.

Here we suppose a carbon atom to be situated at the

Citraconic Acid.   Mesaconic Acid.
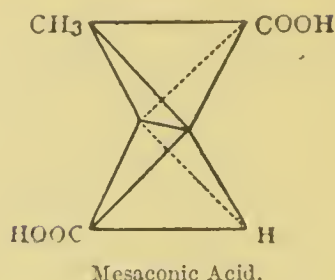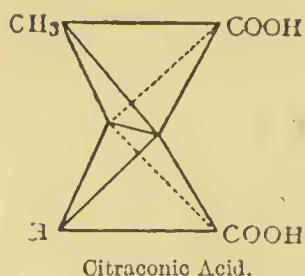
centre of each of the tetrahedra, with its affinities directed to each of the four corners; we then represent a double linkage between the two carbon atoms by joining the tetrahedra along an edge of each. Arranging the hydrogen atoms and methyl and carboxyl groups as shown in the diagrams, we see that citraconic acid has its carboxyl groups disposed in such a manner as to readily give an internal anhydride, whilst this is not the case with mesaconic acid. The change from citraconic to mesaconic acid under the influence of a trace of mineral acid can be represented diagrammatically in the following manner :
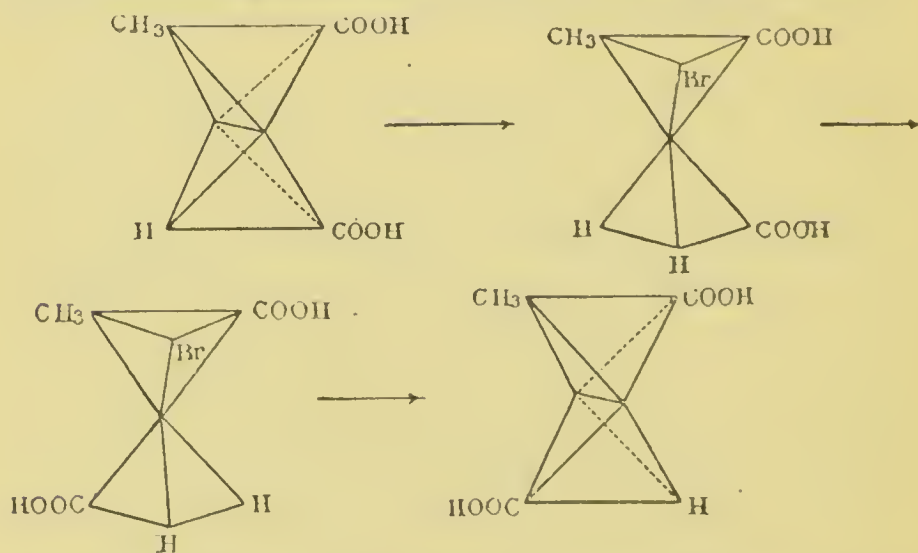
With hydrogen bromide an unstable addition product is first formed, free rotation of the two halves of the mole-

cule then takes place so that the two carboxyl groups may take up a maximum distance from one another, the elements of hydrogen bromide are again split off, and mesaconic acid is produced. Similar explanations may be given when other acids or only water are employed.

Mix in an evaporating basin 1 gram of concentrated nitric acid with 7 c.cm. water. Pour into the mixture 3 grams of citraconic anhydride, and evaporate until red fumes begin to come off. Cool, separate the mesaconic acid which has been formed from the liquid, and recrystallise once from boiling water. Fine colourless needles; melting point 202°; sublimes undecomposed. Requires about 37 parts of water for solution at 15°. Citraconic acid melts, however, at 80°, yields the anhydride when further heated, and dissolves in ·42 parts of water at 15°.

Section V.—Esters of Fatty Acids

The esters of the fatty acids are formed, amongst other methods, by the direct union of the alcohol and acid. Thus, ethyl alcohol and acetic acid give ethyl acetate and water :

$$CH_3 \cdot COOH + C_2H_5OH = CH_3 \cdot COOC_2H_5 + H_2O.$$
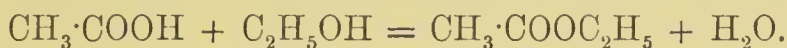
The reaction is, however, never completed in such a case; even when the mixture is heated, a limit is reached beyond which no more of the ester is produced. Better yields of esters are obtained by distilling a mixture of the alcohol and a salt of the acid with concentrated sulphuric acid, or by heating sulphuric acid to 130°, and dropping in a mixture of equivalent quantities of the alcohol and organic acid. In this case we may suppose that the alcohol and sulphuric acid first form an alkyl-sulphuric acid, which then reacts with the organic acid to form an ester whilst

sulphuric acid is regenerated. We can explain these changes by the equations:

$$Alk.OH + H_2SO_4 = Alk.HSO_4 + H_2O.$$
$$Alk.HSO_4 + R \cdot COOH = R \cdot COOAlk. + H_2SO_4.$$
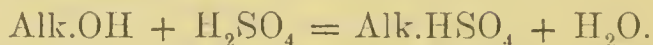
The method can be varied by heating the alcohol, organic acid, and sulphuric acid for some time under reflux.

Very similarly one can saturate a solution of the acid in an excess of the alcohol with gaseous hydrogen chloride, and after some hours' digestion precipitate the ester which has been formed by the addition of water.

Comparatively recently Emil Fischer and Arthur Speier (*Ber.* 1895, **28**, 3252) have shown that better yields of esters may be obtained by a diminution of the amount of mineral acid employed; the reaction is also usually easier to carry out under such circumstances. An example of the employment of Fischer's method will be subsequently given.

Other condensing agents besides free mineral acids may be employed: *e.g.* Girard and Chapoteaut heated a mixture of acid, alcohol, and tin tetrachloride to 100°.

The acid chlorides and anhydrides react readily with alcohols forming esters; the method, though very useful in the case of phenols, is usually avoided when alcohols are being dealt with. Reference to these reactions has previously been made under the head of acetyl chloride and acetic anhydride.

A generally applicable method is to act on the silver (sometimes lead) salt of an organic acid with an alkyl bromide or iodide:

$$R \cdot COOAg + Alk.I = R \cdot COOAlk. + AgI.$$
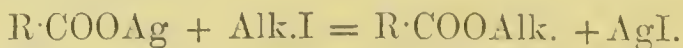
20. **Preparation of Ethyl Acetate** ($CH_3 \cdot COOC_2H_5$).— Mix together in a tubulated retort of 300 c.cm. capacity

130 grams of concentrated sulphuric acid and 65 grams
of ordinary (90 per cent.) alcohol. Connect the retort with
a Liebig's condenser, using a small flask as a receiver.
Now add to the acid and alcohol contained in the retort
100 grams of fused and powdered sodium acetate (see page
104), and mix the contents thoroughly by shaking the
retort. Then bring a water-bath under the retort and
distil the contents as far as possible. The contents of the
receiver are then poured into a separating funnel and
shaken with a strong solution of sodium carbonate to re-
move the alcohol and acetic acid which have distilled over
with the acetic ether. The lower layer is then separated
from the upper layer of acetic ether, which is dried by calcium
chloride without any preliminary washing with water, since
acetic ether is soluble in 11 parts of water. After drying
the acetic ether it is submitted to fractional distillation,
what comes over below 72° being rejected, and that be-
tween 72° and 78° collected as acetic ether. Should it be
desired to obtain the latter quite anhydrous, it is redistilled
over a few strips of metallic sodium.

Where larger quantities of acetic ether are desired,
Pabst's method (*Bull.* 1881, **33**, 350) is better employed, in
which a mixture of 50 c.cm. of concentrated sulphuric acid
and an equal volume of alcohol are heated in a flask of 300
c.cm. capacity (by means of an oil-bath) to 130°-135°,
and then by means of a stoppered funnel introducing in a
continuous stream a mixture of equal volumes (each 500
c.cm.) of alcohol and acetic acid of 93 per cent. strength.
The distillate is treated in the same manner as described
above, and according to Pabst the yield is about 90 per
cent. of the theoretical.

Ethyl acetate is a liquid of pleasant smell and specific

gravity ·92388 at 15°; it boils at 77°.   In aqueous solution it is readily hydrolysed.

21. **Preparation of Ethyl Succinate** $\left(\begin{array}{l}CH_2 \cdot COOC_2H_5 \\ CH_2 \cdot COOC_2H_5\end{array}\right)$.
— Connect a flask of 200 c.cm. capacity to a reflux condenser and charge it with 15 grams of succinic acid, 60 grams of absolute alcohol, and 6 grams of concentrated sulphuric acid.   Heat the mixture to boiling for 4 hours, preferably on the water-bath.   At the end of this time distil off half the alcohol, pour into 200 c.cm. of water and neutralise at once with sodium carbonate.   Pour the mixture into a suitably-sized separating funnel and extract the ethyl succinate by means of ether, separate the ethereal from the aqueous layer, and submit the former to distillation on the water-bath.   When the ether is driven off by this means, continue the heating by the direct flame; water is first driven off together with a small quantity of the ester, then the thermometer rises rapidly, and the ethyl succinate distils between 210° and 225°.   By another fractionation the compound can be obtained pure as a colourless liquid of boiling point 215°.   The yield of ethyl succinate is about equal to the weight of the succinic acid employed.

Section VI.—Aldehydes

The aldehydes are nearly always produced by the oxidation of the corresponding primary alcohols, the process being usually carried out with potassium dichromate and sulphuric acid, e.g.:

$$3CH_3CH_2OH + K_2Cr_2O_7 + 4H_2SO_4 = 3CH_3 \cdot CHO +$$
$$K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O.$$
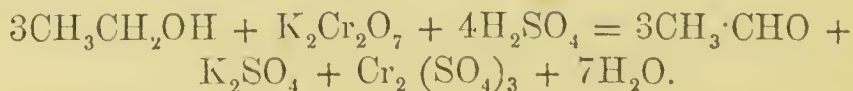
Another way is to distil a mixture of the barium or

calcium salt of an acid with the corresponding formate ; the following reaction then takes place :

$$\begin{matrix} R \cdot COO \\ R \cdot COO \end{matrix} \!\!\! > Ba \ + \ \begin{matrix} H \cdot COO \\ H \cdot COO \end{matrix} \!\!\! > Ba = 2\,BaCO_3 \ + \ 2R \cdot CHO.$$

The aldehydes form addition products with certain compounds and are generally very reactive ; the following reactions may be mentioned :—

(a) With ammonia, aldehydes form crystalline addition products, e.g. :

$$CH_3 \cdot CHO \ + \ NH_3 = CH_2 \cdot CH {\displaystyle <} \begin{matrix} OH \\ NH_2. \end{matrix}$$
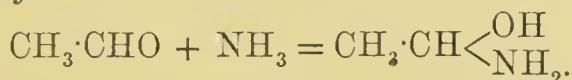
These products lose their ammonia on warming with acids.

(b) The acid sulphites of the alkali metals also combine directly with aldehydes to form beautifully crystalline compounds, e.g. :

$$CH_3 \cdot CHO \ + \ NaHSO_3 = CH_3 \cdot CH {\displaystyle <} \begin{matrix} OH \\ SO_3Na. \end{matrix}$$
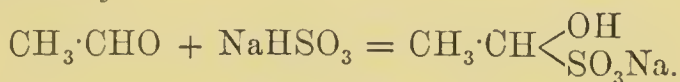
These compounds frequently serve as a means of separating an aldehyde from a mixture ; when they are heated with acids or alkaline carbonates they are again resolved into their components :

$$CH_3 \cdot CH {\displaystyle <} \begin{matrix} OH \\ SO_3\,Na \end{matrix} + \ HCl = CH_3 \cdot CHO \ + \ H_2O \ + \ SO_2$$
$$+ \ NaCl.$$

$$2CH_3 \cdot CH {\displaystyle <} \begin{matrix} OH \\ SO_3Na \end{matrix} + \ Na_2CO_3 = 2CH_3 \cdot CHO \ + \ 2Na_2SO_3$$
$$+ \ CO_2 \ + \ H_2O.$$
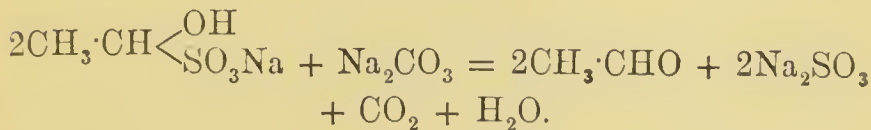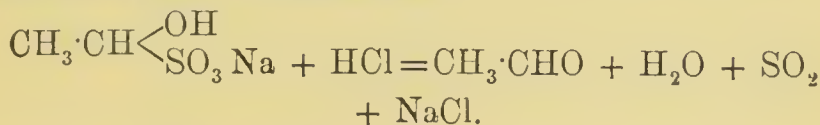
With hydrogen cyanide, cyanhydrins are produced, which on hydrolysis behave as the nitriles of hydroxy acids :

$$CH_3 \cdot CHO + HCN = CH_3 \cdot CH {<}^{OH}_{CN}.$$

$$CH_3 \cdot CH {<}^{OH}_{CN} + HCl + 2H_2O = CH_3 \cdot CH(OH)COOH$$
$$+ NH_4Cl.$$
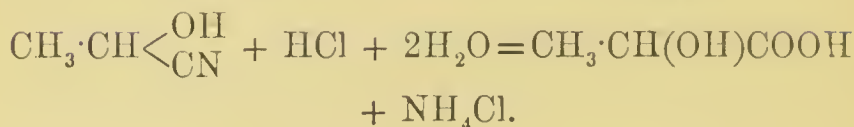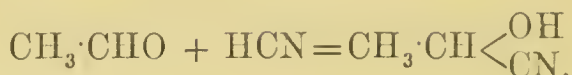
(*d*) Some aldehydes, such as chloral, unite directly with only one molecule of primary monatomic alcohols (thus chloral alcoholate has the formula $CCl_3 \cdot CHO, C_2H_6O$); other aldehydes react with two molecules of an alcohol, with water splitting off at the same time and formation of an acetal :

$$CH_3 \cdot CHO + 2C_2H_5OH = H_2O + CH_3 \cdot CH(OC_2H_5)_2.$$
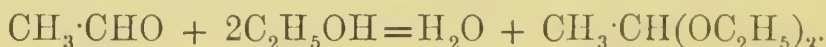
(*e*) In the same way aldehydes combine with two molecules of a mercaptan under the influence of hydrogen chloride, mercaptals being formed :

$$CH_3 \cdot CHO + 2C_2H_5SH = H_2O + CH_3 \cdot CH(SC_2H_5)_2.$$
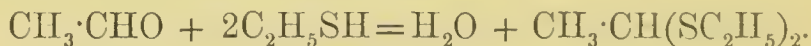
(*f*) Hydroxylamine furnishes oximes, water being eliminated :

$$R \cdot CHO + H_2NOH = R \cdot CH : NOH + H_2O.$$
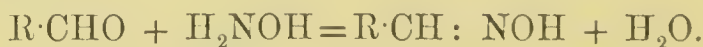
Most of the aldehyde-oximes exist in two isomeric forms; the isomerism is explained by supposing a different arrangement of the atoms in space :

$$
\begin{array}{ccc}
R \cdot C \cdot H & & R \cdot C \cdot H \\
\| & \text{and} & \| \\
NOH & & HON.
\end{array}
$$
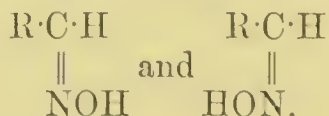
The oximes of the first type (synaldoximes) readily lose the elements of water and pass into the corresponding nitriles ($R \cdot C : N$); this is not the case with those of the second type (anti-aldoximes).

(g) With phenylhydrazine, phenylhydrazones are obtained, $e.g.$:

$$CH_3 \cdot CHO + H_2N \cdot NH \cdot C_6H_5 = CH_3 \cdot CH : N \cdot NH \cdot C_6H_5 + H_2O.$$
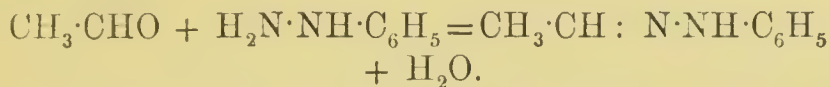
22. **Preparation of Aldehyde and Aldehyde-Ammonia** ($CH_3 \cdot CHO$ and $CH_3 \cdot CH {<}{}^{OH}_{NH_2}$).—Pour 133 grams of concentrated sulphuric acid into 400 grams of water with continual stirring, cool the mixture, add 100 grams of
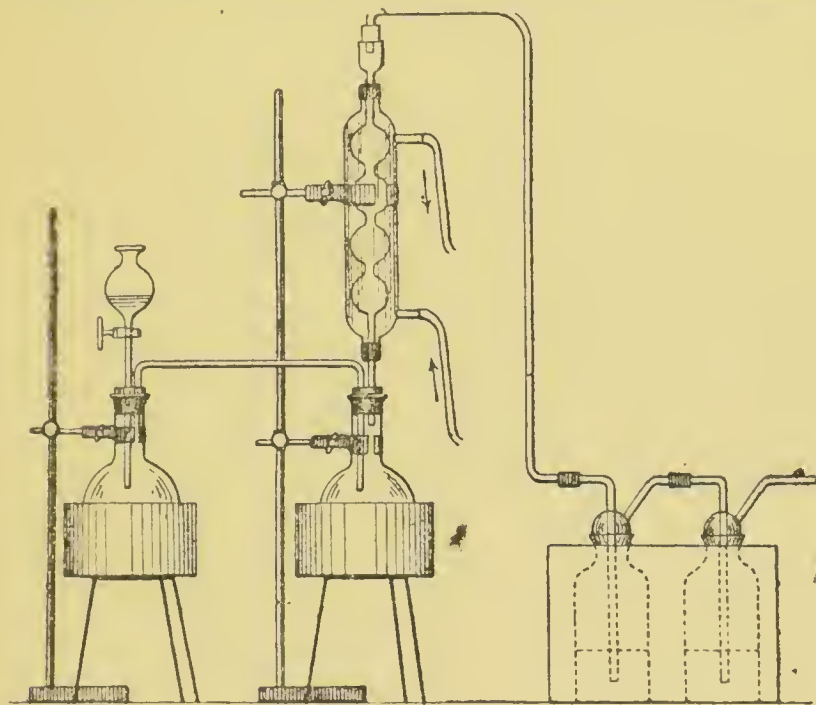
Fig. 57.

alcohol, and cool thoroughly.   Meanwhile fit up the apparatus shown in fig. 57, in which a flask of $1\frac{1}{2}$ litre capacity is fitted with a cork carrying a dropping funnel and leading tube; in this flask place 100 drams of potassium dichromate in pieces about the size of peas, and before pouring

on to the dichromate the mixture of dilute sulphuric acid and alcohol, surround this flask with a freezing mixture of common salt and ice. The leading tube from this flask passes into a second flask which stands in a water-bath and is connected with a Liebig's condenser either of the pattern shown or of the spiral form. This is to ensure more complete condensation of the bye-products than can be effected by means of a condenser of the ordinary type with a straight inner tube. From the top of this condenser a tube passes to two wash-bottles half filled with ether which has been dried first over calcium chloride, then poured off from this, dried again over slices of sodium, and finally distilled. These two bottles serve for the absorption of the aldehyde, an ethereal solution of that compound being obtained. These two wash-bottles must be surrounded with a freezing mixture before the aldehyde is passed into them.

The apparatus being fitted in the way described, and the flask containing the potassium dichromate thoroughly cooled by a freezing mixture, the dilute sulphuric acid and alcohol are allowed to flow in by the dropping funnel in small quantities at a time. The addition must be made sufficiently gradually to avoid heating and consequent boiling. Meanwhile the water-bath in which the second flask is placed is raised to 50° and the reflux condenser fed with water at about 30°. When all the liquid has been added to the dichromate in the first flask, the mixture is allowed to stand about half an hour; the freezing mixture is then removed and the contents of the flask almost immediately begin to boil (the boiling point of acetaldehyde is 21°). When the boiling begins to slacken off the flask may be warmed, gently at first and afterwards more strongly. In this way a mixture containing in addition

to the aldehyde various other substances (alcohol, acetal, water, and ethyl acetate) will be driven over, but, on account of the second flask and the reflux condenser attached to it, only the first of these—the aldehyde—will pass into the anhydrous ether, by which it is readily absorbed.

When the reaction is completed the contents of the two washing-bottles are saturated with dry ammonia gas prepared from *liquor ammoniæ* by heating and drying the gas evolved with a lime-tower. For the purpose of saturation, disconnect the two washing-bottles from the reflux condenser—but do not remove them from the freezing mixture—connect with the ammonia apparatus, and pass in the gas. As the ammonia is led into the cooled ethereal solution, crystals of aldehyde-ammonia separate ; when the saturation is complete disconnect the ammonia gas, fit stoppers made of connection tubing and glass rod over the tubes of the washing-bottles, and allow to stand for twelve hours. Filter off the mass of crystals which has separated as completely as possible with the aid of the pump, wash two or three times with small quantities of absolute ether, and dry the crystals on filter paper in the air.

About 35 grams of aldehyde-ammonia should be obtained ; melting point 70°–80°. Preserve the crystals in a well-stoppered bottle.

Section VII.—Ketones and Ketonic Acids

The ketones are prepared in a variety of ways, the most common being the distillation of the calcium or preferably barium salt of an acid, *e.g.* :

$$\begin{array}{c} CH_3 \cdot COO \\ CH_3 \cdot COO \end{array}\!\!>Ca = CaCO_3 + \begin{array}{c} CH_3 \\ CH_3 \end{array}\!\!>CO.$$

M
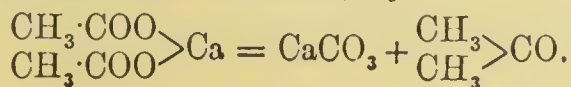
If a mixture of the salts of two different acids is taken, a mixed ketone is the result:

$$\begin{matrix} CH_3 \cdot COO \\ CH_3 \cdot COO \end{matrix} \Big> Ca \ + \ \begin{matrix} C_2H_5 \cdot COO \\ C_2H_5 \cdot COO \end{matrix} \Big> Ca = 2CaCO_3$$

$$+ \ 2 \begin{matrix} CH_3 \\ C_2H_5 \end{matrix} \Big> CO.$$
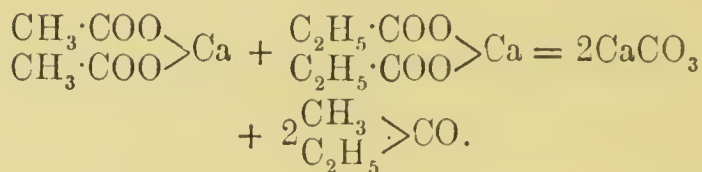
Ketones are also formed by the oxidation of secondary alcohols and tertiary oxyacids:

$$(C_nH_{2n+1})_2CH(OH) + O = H_2O + (C_nH_{2n+1})_2CO.$$
$$(C_3H_7)_2C(OH)CO_2H + O = CO_2 + H_2O + (C_3H_7)_2CO.$$
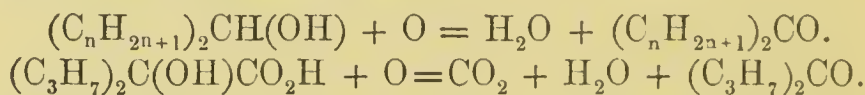
The homologues of acetylene are able to add the elements of water under the influence of various reagents; thus, when allylene is passed into an aqueous solution of mercuric chloride heated to 90°–95°, acetone is produced:

$$CH_3 \cdot C : CH + H_2O = CH_3 \cdot CO \cdot CH_3$$

The esters of the ketonic acids undergo the ketonic (in contradistinction to the acidic) decomposition when boiled with dilute alkalies.   Ethyl acetoacetate yields under these circumstances carbon dioxide, alcohol and acetone:

$$CH_3 \cdot CO \cdot CH_2 \cdot COOC_2H_5 + H_2O = CH_3 \cdot CO \cdot CH_3 + C_2H_5OH$$
$$+ CO_2.$$
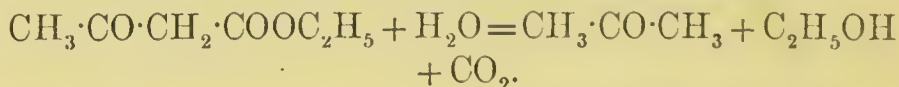
23. **Preparation of Acetone** ($CH_3 \cdot CO \cdot CH_3$).—Dissolve 50 grams of barium carbonate in 30 grams of glacial acetic acid which has been diluted with three times its volume of water, stirring the mixture meanwhile and aiding the reaction at the end by warming on the water-bath.   When the evolution of carbon dioxide has quite ceased raise the solution to boiling, filter through a plaited filter, pour the filtered liquid into an evaporating basin and evaporate to complete dryness.   Then expel the remaining water of crystallisation by heating to 150°, powder the saline mass

and introduce it into a retort of 300 c.cm. capacity.   Connect this with a Liebig's condenser through the outer tube of which a stream of thoroughly cold water is passing, and arrange at the end a small flask as receiver.[1] Now heat the contents of the retort with a fairly large Bunsen flame to which a rotatory motion is communicated, so as to ensure as far as possible an even heating of the retort and its contents. When no more liquid distils over into the receiver, add a few pieces of granular calcium chloride, shake up, cork, and allow to stand for an hour, then pour the liquid into a distilling flask and submit to fractional distillation.   Acetone comes over as a colourless liquid boiling at 56° C.

Pour 1 c.cm. of acetone into a test-tube and add a small quantity of a saturated solution of acid sodium sulphite. Colourless leaflets of the bisulphite compound having the composition $(CH_3)_2C(OH)SO_3Na$ separate out.   If these are freed from excess of sodium bisulphite solution by pouring on to porous earthenware and then warmed with a few drops of caustic soda solution, the smell of acetone will be noticed.

24. **Preparation of Pyruvic Acid** $(CH_3 \cdot CO \cdot COOH)$.—In this compound we have an example of the occurrence of both a ketonic carbonyl and a carboxyl group in the same molecule; it therefore shows the properties both of an acid and a ketone.   Mix together and powder thoroughly 50 grams of dried tartaric acid and 100 grams of commercial potassium bisulphate.[2] Place the mixture in a retort of about 500 c.cm. capacity, connect this with a condenser the end of which passes into a fractionating flask as described

---

[1] The Liebig's condenser should be fairly long, as acetone is very volatile.

[2] This consists very largely of potassium anhydrosulphate, $K_2S_2O_7$.

in the case of citraconic anhydride.   The tube of the frac-
tionating flask is, as in the case mentioned, connected with
a tube which passes into a Bunsen burner to effect the com-
bustion of objectionable gases.   Now heat the mixture of
tartaric acid and potassium bisulphate gently until all is
melted and thoroughly mixed, then continue the warming
with a large flame, whereby the liquid takes a very dark
brown colour and bubbles of gas begin to come off.   Con-
tinue the distillation rapidly, taking care that none of the
liquid boils over into the condenser, and discontinue heating
when no more distillate is seen to condense in the condenser.
The residue in the retort consists of carbonaceous material
and potassium salts, which, as in the preparation of citra-
conic anhydride, are extracted only with difficulty.   The
acid distillate which has been received in a fractionating
flask is submitted to successive distillations in order to
obtain the pyruvic acid in a pure condition.

Fit the distilling flask with a thermometer and connect
it with a condenser, heat the flask and its contents, collect-
ing all that comes over before $140°$ in a small beaker.
When the temperature of $140°$ is reached, replace the
beaker by a distilling flask, in which collect all that
comes over between the temperatures of $140°$ and $180°$.
Fit this flask in turn with cork and thermometer, and
from it distil the liquid a second time. In this case collect
the distillate below $150°$ in the beaker, and at this tem-
perature substitute a distilling flask, collecting in it the
fraction obtained between $150°$ and $170°$. By a third
rectification of this distillate, and collection of the acid
which distils between $165°$ and $170°$, nearly pure pyruvic
acid (contaminated by traces of water) may be obtained as
a nearly colourless liquid, easily soluble in water and of
specific gravity $1·288$. From 50 grams of tartaric acid,

about 15 grams of pyruvic acid should be obtained ; the reaction may be expressed by the equation :

$$\begin{matrix} COOH \\ | \\ CHOH \\ | \\ CHOH \\ | \\ COOH \end{matrix} = CO_2 + H_2O + \begin{matrix} CH_3 \\ | \\ CO \\ | \\ CH_3 \end{matrix}$$
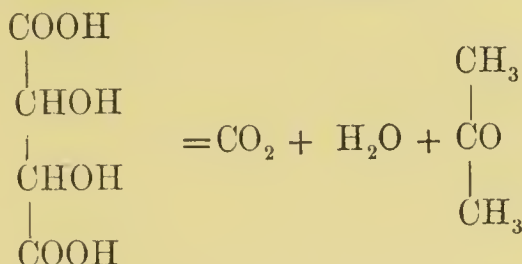
The aqueous solution received in a beaker during the three distillations contains appreciable quantities of pyruvic acid. If phenylhydrazine dissolved in dilute acetic acid be added to this aqueous distillate, a lemon yellow precipitate of pyruvic acid phenylhydrazone will be obtained. It is formed according to the equation :

$$\begin{matrix} CH_3 \\ | \\ CO \\ | \\ COOH \end{matrix} + C_6H_5 \cdot NH \cdot NH_2 = H_2O + \begin{matrix} CH_3 \\ | \\ C : N \cdot NH \cdot C_6H_5 \\ | \\ CH_3. \end{matrix}$$
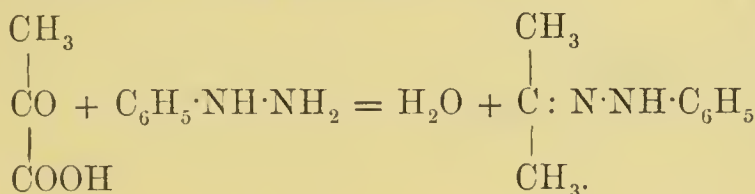
When recrystallised from dilute alcohol the pyruvic acid phenylhydrazone forms pale yellow needles which melt at 169°.

25. **Preparation of Ethyl Acetoacetate** ($CH_3 \cdot CO \cdot CH_2 \cdot COOC_2H_5$).—Weigh out 100 grams of freshly distilled ethyl acetate into a flask of about 300 c.cm. capacity, connect this with a reflux condenser cooled thoroughly by running water, and introduce into the ethyl acetate 4 grams of sodium which have been cut into very thin fragments. During the addition of the sodium, the flask containing the ethyl acetate should be cooled from the outside by immersing it in a basin of cold water. The sodium at first begins to dissolve somewhat rapidly, with

the result that the contents of the flask begin to boil ; as soon as the evolution of heat decreases, and the first reaction is finished, remove the flask from the cold water, place it on a water-bath, and heat until all the sodium has gone into solution. As soon as this is effected, distil off the excess of ethyl acetate on the water-bath, and whilst the liquid is still warm add 56 grams of 50 per cent. acetic acid (*i.e.* 28 grams 100 per cent. acetic acid diluted with an equal weight of water). Now allow the mixture to cool, add a further 25 grams of water, transfer to a separating funnel and shake thoroughly. On standing, the liquid separates into two layers, of which the upper contains the ethyl acetoacetate ; wash this by shaking with small quantities of water, transfer it to a round-bottomed flask ; fit this with a two-bulbed Wurtz's tube and submit the liquid to fractional distillation (see fig. 58). Collect the liquid which distils over in 5 fractions, (i.)100°–130°, (ii.) 130°–165°, (iii.) 165°–175°, (iv.) 175°–185°, (v.) 185°–200°. Of these fractions, that between 175° and 185° should be the largest, and consists of nearly pure ethyl acetoacetate. A further quantity of this ester may be obtained by systematically subjecting the other fractions to fractional
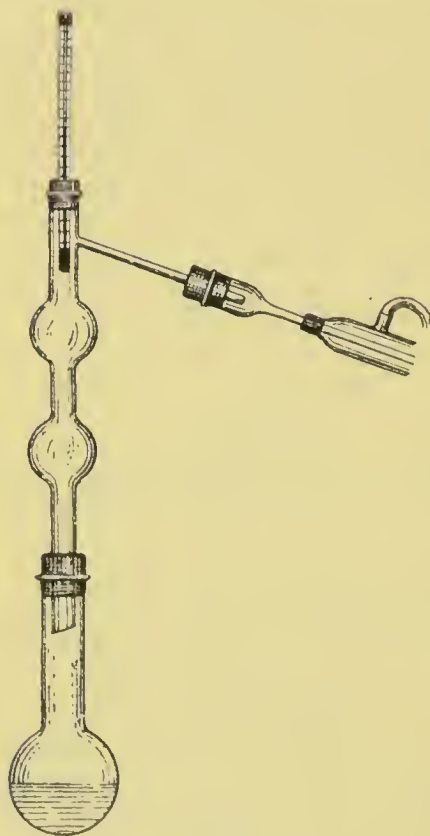
FIG. 58.

distillation, using the Wurtz tube also in this case. The fractionation may be repeated three times; it is better, however, not to go further, since continued heating of ethyl acetoacetate ends in the formation of products of lower boiling point and dehydracetic acid. Yield, 12 to 14 grams.

Ethyl acetoacetate is a colourless liquid: specific gravity 1·03 (at 5° C.); boiling point 182°.

The reaction of the sodium on the ethyl acetate is often expressed by the equation :

$$2CH_3 \cdot COOC_2H_5 + 2Na = CH_3 \cdot CO \cdot CHNa \cdot COOC_2H_5$$
$$+ C_2H_5ONa + H_2 ;$$
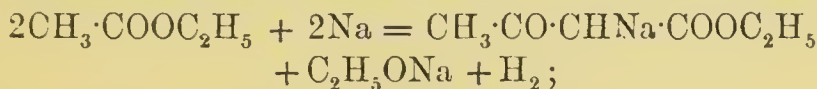
i.e. the sodium derivative of ethyl acetoacetate and sodium alcoholate are produced. Claisen and Lowman (*Ber.* 1887, **20**, 651) consider, however, that the change is brought about by the formation of small quantities of sodium ethyl-ate,[1] which forms with ethyl acetate an addition product, sodium diethyl orthoacetate :

$$CH_3 \cdot COOC_2H_5 + NaOC_2H_5 = CH_3 \cdot C{\overset{\displaystyle OC_2H_5}{\underset{\displaystyle ONa}{-OC_2H_5}}}.$$
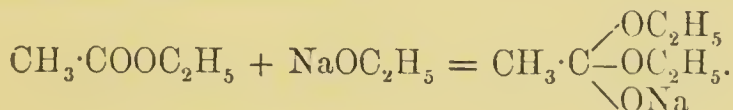
This product then reacts with a second molecule of ethyl acetate as follows :

$$CH_3 \cdot C{\overset{\displaystyle OC_2H_5}{\underset{\displaystyle ONa}{-OC_2H_5}}} + CH_3 \cdot COOC_2H_5 =$$
$$CH_3 \cdot C(ONa) : CH \cdot COOC_2H_5{}^2 + 2C_2H_5OH.$$
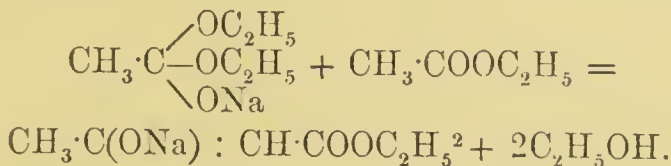
The subsequent addition of the dilute acetic acid is to

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[1] Ethyl acetoacetate may be produced by the action of sodium ethylate on ethyl acetate.

[2] Tautomeric form of $CH_3 \cdot CO \cdot CHNa \cdot COOC_2H_5$.

effect the removal of the sodium in the sodium derivative of the acetoacetic ether and to replace it by hydrogen, thus :

$$CH_3 \cdot CO \cdot CHNa \cdot COOC_2H_5 + CH_3 \cdot COOH$$
$$= CH_3 \cdot CO \cdot CH_2 \cdot COOC_2H_5 + CH_3 \cdot COONa.$$
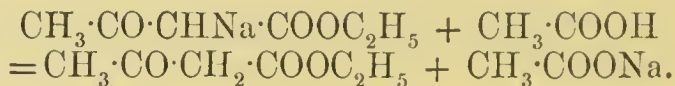
The sodium derivative of acetoacetic ether can at any time be easily produced by dissolving the ester in absolute alcohol in which the calculated quantity of sodium has been dissolved.   By treatment of the resulting compound with the halogen compound of an alkyl group, the sodium is replaced by the alkyl—*e.g.* :

$$CH_3 \cdot CO \cdot CHNa \cdot COOC_2H_5 + C_2H_5I = NaI +$$
$$CH_3 \cdot CO \cdot CH(C_2H_5) \cdot COOC_2H_5.$$
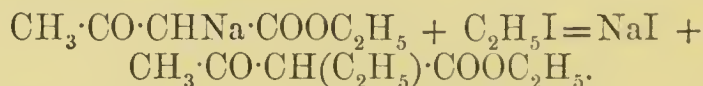
A second alkyl group can now be introduced into the molecule by successive treatment with sodium ethylate and an alkyl halide, the compound so formed being of the type $CH_3 \cdot CO \cdot CRR' \cdot COOC_2H_5$.

When acetoacetic ether is boiled with a dilute alkali or dilute sulphuric acid, it undergoes the ketonic fission yielding acetone, carbon dioxide, and ethyl alcohol.   Its alkyl derivatives undergo a similar decomposition, and hence ethyl acetoacetate may be used for the synthesis of complex ketones :

$$CH_3 \cdot CO \cdot CRR' \cdot COOC_2H_5 + H_2O = CH_3 \cdot CO.CHRR'$$
$$+ CO_2 + C_2H_5OH.$$
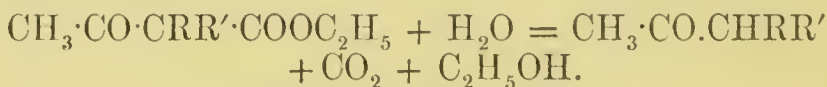
On the other hand, strong solution of caustic potash brings about the acidic fission by which means the synthesis of derivatives of acetic acid may be effected :

$$CH_3 \cdot CO \cdot CRR' \cdot COOC_2H_5 + 2KOH = CH_3 \cdot COOK$$
$$+ CHRR' \cdot COOK + C_2H_5OH.$$

Ethyl acetoacetate may also be utilised for the syn-

thesis of ketonic dibasic acids—*e.g.* ethyl chloracetate and the sodium derivative of ethyl acetoacetate give diethyl aceto-succinate :

$$CH_3 \cdot CO \cdot CHNa \cdot COOC_2H_5 + Cl \cdot CH_2 \cdot COOC_2H_5$$

$$= NaCl + \quad \begin{array}{c} CH_3 \cdot CO \cdot CH \cdot COOC_2H_5 \\ | \\ CH_2 \cdot COOC_2H_5. \end{array}$$
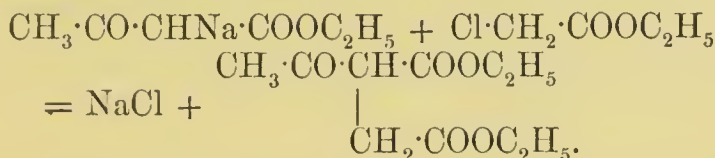
When the above-mentioned sodium derivative is treated with iodine, diethyl diaceto-succinate is produced :

$$2CH_3 \cdot CO \cdot CHNa \cdot COOC_2H_5 + I_2 = 2NaI$$

$$\begin{array}{c} CH_3 \cdot CO \cdot CH \cdot COOC_2H_5 \\ | \\ CH_3 \cdot CO \cdot CH \cdot COOC_2H_5. \end{array}$$
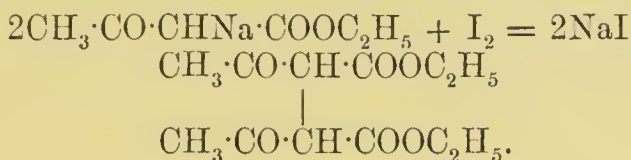
The application of ethyl acetoacetate in the synthesis of closed chain compounds in which nitrogen forms a part will be referred to later.

26. **Preparation of Ethyl Aceto-ethyl-acetate** ($CH_3 \cdot CO$ $CH(C_2H_5) \cdot COOC_2H_5$).—Provide a flask with a reflux condenser, and run into the flask 30 c.cm. of 96 per cent. alcohol. Dissolve in the alcohol 2·3 grams of sodium ; when the latter has gone into solution cool the flask and its contents, then add 13 grams of ethyl acetoacetate, shake the contents of the flask, pour in immediately 15·6 grams of ethyl iodide and heat the mixture to boiling on the water-bath under reflux. After two and a half hours, dip a glass rod into the solution, and by its aid bring a drop of the solution on to red litmus paper. Moisten the spot with a drop of water ; if no alkaline reaction be noted, the conclusion may be drawn that all the sodium derivative of ethyl acetoacetate has been acted on. If an alkaline reaction is however detected, the heating must be continued until this disappears.

Then distil off the alcohol as completely as possible, pour the residue into a separating funnel, rinse the contents of the flask with 30 c.cm. of water, add this to the liquid in the funnel, shake thoroughly, and allow the liquid to separate into two layers. Run the aqueous solution off into a small beaker, the upper layer into a small flask. Transfer the aqueous solution once more to the funnel, extract with 30 c.cm. ether, separate the two layers, adding the ethereal solution to the contents of the flask. Now dry the ethereal solution of the ester with dehydrated sodium sulphate, transfer to a distilling flask and rectify. The distillate obtained between 190° and 196° may be taken as pure ester; the yield should be about 11 grams.

Section VIII.—Hydroxy Derivatives of Ketones and Aldehydes

These compounds contain both alcoholic and aldehydic or ketonic groups. The simplest possible compounds of this type are formulated as follows :

$$
\begin{array}{cccc}
CH_2 \cdot OH & CH_2OH & CH_2OH & CH_2OH \\
| & | & | & | \\
CHO & CO & CHOH & CO \\
 & | & | & | \\
 & CH_3 & CHO & CH_2OH \\
\end{array}
$$

Glycollic aldehyde.　Hydroxyacetone.　Dihydroxypropionic　Dihydroxyacetone.
　　　　　　　　　　　　　　　　　(glyceric) aldehyde.
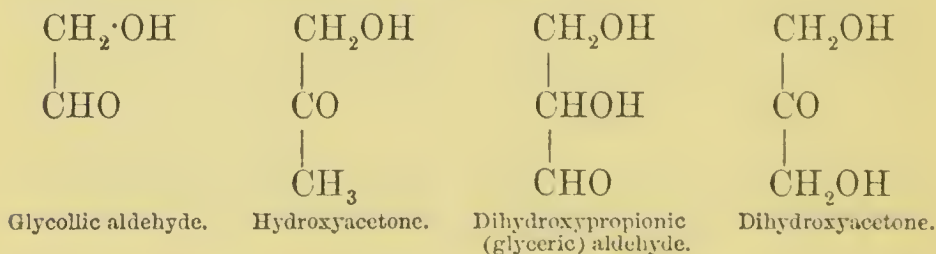
A mixture of the last two compounds may be obtained by the gentle oxidation of glycerine. These comparatively simple carbohydrates ($C_3H_6O_3$) easily polymerise; thus acrose may be obtained according to the equation:

$$2C_3H_6O_3 = C_6H_{12}O_6.$$
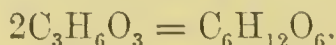
The acrose so obtained may, by a series of reactions,

be transformed into the isomeric glucose which occurs in nature as grape sugar. Glucose is in fact nothing more than a pentahydroxyhexoic aldehyde, whilst fructose (fruit sugar, formerly spoken of as levulose) is an isomeric ketone. We may formulate these two compounds as follows:
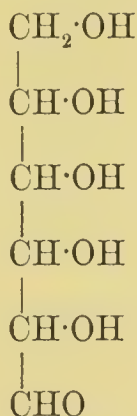
$$
\begin{array}{cc}
CH_2 \cdot OH & CH_2 \cdot OH \\
| & | \\
CH \cdot OH & CH \cdot OH \\
| & | \\
CH \cdot OH & CH \cdot OH \\
| & | \\
CH \cdot OH & CH \cdot OH \\
| & | \\
CH \cdot OH & CO \\
| & | \\
CHO & CH_2OH \\
\text{Glucose.} & \text{Fructose.}
\end{array}
$$
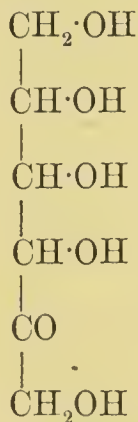
A large number of isomeric substances are known, some occurring in nature, others artificially prepared; these have constitutional formulae, which when given the ordinary plane representation, such as above, appear identical with those of glucose and fructose. The isomerism depends on the arrangement of the carbon atoms in space. We notice that in the molecule of glucose we have four asymmetric carbon atoms, i.e. carbon atoms, each of which is attached to four different atoms or groups. Similarly, fructose possesses three asymmetric carbon atoms, and on examining the behaviour of these substances towards polarised light we find that they are both optically active, glucose rotating the plane of polarisation towards the right, fructose, however, towards the left. The measurement of the optical activity of such substances is of great importance, both in their recognition and in the

elimination of their constitution. We shall, therefore, describe here the measurement of the specific and molecular rotation of cane-sugar.

Molecular Rotation of Cane-Sugar $(C_{12}H_{22}O_{11})$.—Cane-sugar is a dextrorotatory substance ; when hydrolysed by boiling with dilute acids it is converted into a mixture of equal molecules of glucose and fructose :

$$C_{12}H_{22}O_{11} = C_6H_{12}O_6 + C_6H_{12}O_6.$$

This hydrolysis is frequently spoken of as ' inversion,' since the resulting solution is laevorotatory, fructose being more strongly laevorotatory than glucose is dextrorotatory.

Finely powder about 10 to 12 grams of cane-sugar, thoroughly dry this by allowing it to stand, spread out on a clock glass in a desiccator over sulphuric acid for 12 to 24 hours. Weigh out accurately about 10 grams of the carefully dried substance into a measuring flask of 100 c.cm. capacity, add cold distilled water to bring the sugar into solution, and then carefully make up to volume. Allow the solution to stand some hours before making the determination of the optical activity, and also be careful that the distilled water with which the solution is made up does not contain any traces of acid.

The polarimeters used for the determination of the rotation vary considerably in construction. We shall deal here with one of the simplest forms of the instrument constructed by Carl Zeiss, of Jena.[1]

In this instrument p is the polarising Nicol prism, a the analyser, and q the quartz plate. If the adjustment of the instrument is correct, the pointer d should indicate the zero point on the divided scale C when the tube A is re-

---

[1] The English agent is C. Baker, 244 High Holborn, London.

moved from the outer casing B or is in place filled with distilled water, the two halves of the quartz plate having an identical reddish violet hue when the tube E is directed towards the clear sky or the shade of a lamp. The eye is always placed at the opening of the tube D. The length of the tube A in the instrument described is exactly 20 cm.

Supposing the instrument to be in adjustment, turn the polariser p on one side; it revolves about the pivot F. Take out the tube A and unscrew one of the glass plates, s. Rinse the tube out with some of the sugar solution of known strength, and then fill it completely with the solution, holding the tube in a vertical position and taking care that no air-bubbles remain in the tube.

Then screw on the glass plate s, replace the tube
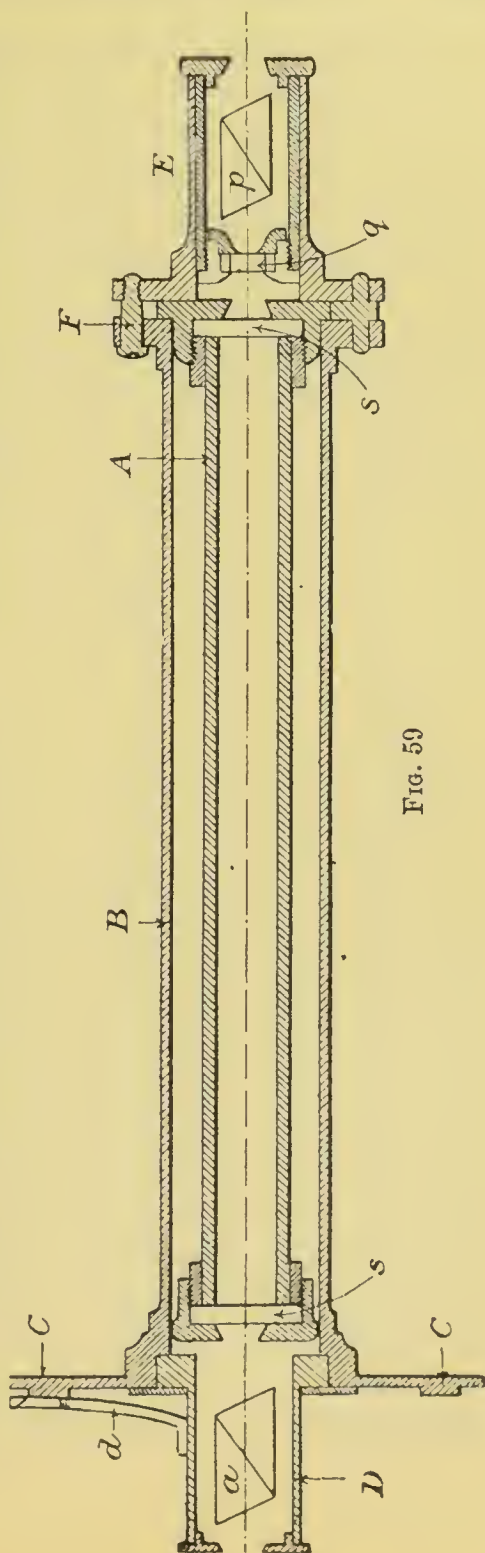
Fig. 59

in the outer casing B, and return the polariser to the position
shown in the diagram.   Directing E, as before, to the clear
sky or a lamp shade, it will be found that the two halves of
the quartz plate no longer appear of an equal shade and D
will have to be rotated through a certain angle before the two
halves of the quartz plate appear of an equal reddish violet
tint.   The angle through which D has to be turned will
measure the angle through which the plane of polarisation
has been rotated by the sugar solution contained in A.

Another reading can be taken by turning the analyser
through two right angles; the difference in readings for no
rotation of the plane of polarisation, and when the sugar
solution is inserted between polariser and analyser, being
noted also for this position.   Take the mean of the two
readings and regard this as the rotation for the solution in
question.

Make a second determination of the rotation after re-
filling the tube with the solution, so as to get as reliable a
value as possible.

When these readings have been taken, dilute 50 c.cm. of
the solution and repeat the observations; it will be observed
with a delicate instrument that the rotation is not exactly
proportional to the amount of substance dissolved, but that
the effect slightly decreases for increased concentration.

To calculate the value of $[a]$, the specific rotation, we
proceed in the following manner.

The specific rotation of an active substance is defined
as that rotation of the plane of polarisation which is
effected by 1 gram of the substance if this takes up the
space of 1 c.cm., and produces its effect on the plane of
polarisation, in a thickness of 1 dm.

The tube A in the apparatus described is made exactly
2 decimetres in length.   Suppose the weight of sugar we

have made up to a solution of 100 c.cm. to be w grams ; if a be the observed rotation, we obviously have

$$[a] = \frac{100\,a}{2 \times w}.$$

For cane-sugar this number should come out to about 66·5°.

To calculate the molecular rotation we have to remember that this is the rotation which one molecular weight of the substance expressed in grams would effect if the gram molecular weight occupied 1 c.cm., and was used in a thickness of 1 mm. If m be the molecular weight of the substance and $[m]$ the molecular rotation,

$$[m] = \frac{m \times 100 \times a}{200 \times w}$$

$$= \frac{ma}{2w}.$$

In making these determinations of rotation, the temperature at which the observations are made should be noted, since the amount by which the plane of polarisation is rotated depends on the temperature of solution. For a description of the more elaborate forms of polarimeters the reader is referred to Traube's 'Physikalisch-Chemische Methoden,' pp. 195–210.

A method by which the sugars are sometimes estimated depends on the power many of them possess of reducing an alkaline cupric solution (Fehling's solution). Since this process is usually given in the text-books on volumetric analysis the reader is referred to them for further information on this subject.

CHAPTER VI

THE AROMATIC HYDROCARBONS AND THEIR DERIVATIVES

THE chief source of the aromatic hydrocarbons is coal-tar, from which several of the more important compounds are separated by fractional distillation, washing of the fractions so obtained with alkalies and acids to remove substances of acid and basic character respectively, and further purification in which fractional distillation plays a large part. A few of the aromatic hydrocarbons may be obtained by direct synthetical processes from fatty materials. Thus acetylene when conducted through a red-hot tube gives benzene (C_6H_6) amongst other products. This latter hydrocarbon, benzene, is to be looked on as the parent substance of the aromatic series, and may be represented by one of the three following formulæ :
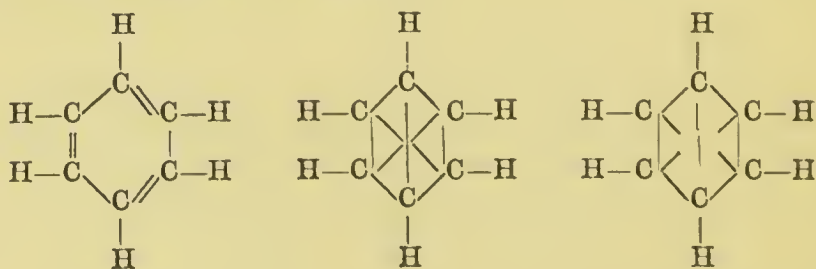
Another synthesis of a hydrocarbon of the aromatic series from fatty materials is the synthesis of mesitylene from acetone.

Section I.—Hydrocarbons and their Nitration

27. **Synthesis of Mesitylene from Acetone.**—Place 70 grams of dry sand in a tubulated retort of 600–800 c.cm. capacity. Pour on to this 100 c.cm. of commercial acetone. 100 c.cm. of strong commercial sulphuric acid are poured into a beaker which is cooled by standing it in a vessel containing water; dilute this acid with 50 c.cm. of water which should be added slowly with continuous stirring. The mixture of sulphuric acid and water is thoroughly cooled, and then poured in a continuous thin stream very slowly into the sand and acetone contained in the retort. During the addition of the acid stand the retort in water so as to effect outside cooling. The stopper is now inserted in the tubulus of the retort, which is allowed to stand at the ordinary temperature for twenty-four hours. At the end of this time clamp the retort to a stand, supporting it underneath with wire gauze, and distil its contents. At first acetone and water come over; when any oil appears the receiver is changed and the crude mesitylene is collected apart. When as much hydrocarbon as possible has been collected add caustic soda solution to the contents of the receiver until a strong alkaline reaction is obtained; permanent on shaking. Transfer the soda and mesitylene to a separating funnel, and shake thoroughly. Allow the contents of the separating funnel to form two layers, remove the lower one, testing to see that it is still alkaline (if not, the soda washing must be repeated with a fresh quantity of caustic soda solution). The mesitylene which is left in the receiver is then washed four or five times with fresh quantities of water, the hydrocarbon (sp. gr. ·8694 at $\dfrac{9\cdot 8^\circ}{4^\circ}$) always

N

forming the upper layer. Finally distil the hydrocarbon from a small distilling flask, collecting what comes over between 160° and 170° in a small flask apart from the rest ; add a few pieces of metallic sodium to effect complete dehydration, shaking from time to time ; then pour the mesitylene into a distilling flask, heat and collect again all that comes over between 160° and 170°.

Pure mesitylene boils at 163° ; the substance with this boiling point can only be obtained from the acetone product after repeated fractionation. The main course of the reaction between the acetone and the sulphuric acid may be represented by the equation :

$$\begin{array}{c} CH_3 \\ | \\ CO \\ CH_3 \quad \diagdown CH_3 \\ | \\ CO \\ CH_3 \diagup \quad CO-CH_3 \\ CH_2 \diagup \end{array} = 3\,H_2O \; + \; \begin{array}{c} CH_3 \\ | \\ C \\ H-C \diagup \diagdown C-H \\ | \qquad\qquad | \\ CH_3-C \diagdown \diagup C-CH_3 \\ C \\ | \\ H \end{array}$$
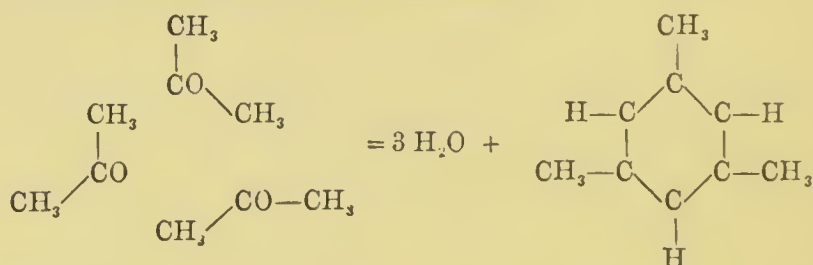
Nitro Derivatives of Benzene.—When benzene is treated with nitric acid, direct replacement of hydrogen by a nitro-group takes place. This behaviour is somewhat characteristic of the aromatic hydrocarbons and their derivatives ; very few nitro-derivatives of the fatty series have been obtained by the direct action of nitric acid. (Cf. p. 124.)

28. **Preparation of Mononitrobenzene** $(C_6H_5NO_2)$.—Mix together in a flask of about 250 c.cm. capacity 40 c.cm. of concentrated sulphuric acid and 40 c.cm. of concentrated nitric acid (sp. gr. 1·42). The sulphuric acid should first be introduced into the flask and the nitric acid added in small quantities, cooling the flask from the outside by running water after each addition. The flask and its contents are placed in a vessel containing water, so that the

material may be kept cool throughout the experiment : 25 grams of pure benzene are weighed out into a small beaker and added gradually to the acid mixture; after each addition of 2 or 3 c.cm. the flask is shaken to effect a thorough mixture and introduced into the cold water again. The temperature of the mixture should be tested from time to time with a thermometer; be careful that this does not go above 50° C. When all the benzene has been added the flask is transferred to a water-bath and heated to a temperature of 75°–80° for an hour, a thermometer being placed in the mixture. The mixture is then poured into three times its volume of water, and more water added until the nitrobenzene sinks easily through the diluter acid and collects as a yellow oil at the bottom of the beaker. Separation is effected in the separating funnel, in which the nitrobenzene is thoroughly washed several times with fresh quantities of water. The nitrobenzene layer is finally separated by the funnel as completely as possible from water, run into a small flask and warmed on the water-bath with calcium chloride until the liquid is quite clear. The nitrobenzene is then decanted into a fractionating flask and distilled; collect what comes over at 205°–210°. If the washing with water has not been thorough, an explosion will probably occur during this distillation. About 30 grams of mononitrobenzene should be obtained.

29. **Preparation of Dinitrobenzene** $(C_6H_4(NO_2)_2 1 : 3)$.— Fifteen c.cm. of concentrated sulphuric acid and 10 c.cm. of fuming nitric acid (sp. gr. 1·5) are mixed in a small flask of about 120 c.cm. capacity. To this mixture 10 grams of nitrobenzene are added in small quantities, no special precautions as to cooling being taken. The flask and its contents are now heated to 100° on the water-bath for half an hour, just raised to the boil over wire gauze and poured into a

large excess of cold water (200–300 c.cm.) with continual
stirring. The dinitrobenzene separates out in a crystal-
line condition, is filtered and well washed with cold water,
dissolved in hot alcohol, filtered through a plaited filter and
allowed to separate out slowly on cooling. The collected,
washed and dried substance should weigh about 11 grams
and melt at 90°.

By very energetic nitration a third nitro group may be
introduced into the benzene molecule.

In both the preceding cases the nitration was effected by
nitric acid in presence of sulphuric acid. Frequently such
treatment would be far too energetic; thus, when mononitro-
phenols are required, not only is the sulphuric acid omitted
but the nitric acid is itself diluted. Many modifications
of the process are also in use : in the case of primary aro-
matic bases, for example, special precautions have to be
taken, otherwise a useless tarry mass results. Generally
the amido group is ' protected ' from the destructive action
of the nitric acid by replacing one of its hydrogen atoms
with an acetyl group. A method which has been con-
siderably employed of late years consists in dissolving the
base in a considerable excess of strong sulphuric acid,
cooling thoroughly and pouring in the calculated quantity
of nitric acid, itself diluted with sulphuric acid.

We also note in the preparation of dinitrobenzene that
the second nitro group enters in the meta-position rela-
tively to the first. Similarly, if nitro-benzene be chlorinated,
the chlorine atom enters into the meta-position to the nitro
group. The nitro group when introduced into the benzene
nucleus conditions the entrance of a second group in the
meta position. On the other hand, if we submit chlor-
benzene to the action of nitric acid we obtain a mix-
ture of ortho and paranitrochlorbenzenes. Just as the

nitro group conditions the entrance of the second substituent in the meta-position, so the chlorine atom conditions the formation of ortho and para derivatives.   It should be added that the meta-dinitrobenzene is accompanied in its formation with small quantities of the ortho and para compounds, but these are removed by the process of crystallisation.

Groups which, like the nitro group, condition the formation of a meta-derivative are CO_2H, COH, SO_3H, and CN. On the other hand, a mixture of ortho and para compounds results by suitable treatment of benzene in which one of the hydrogen atoms has been replaced by Cl, Br, I, NH_2, NHC_2H_3O, or CH_3

SECTION II.—REDUCTION OF NITRO COMPOUNDS

The Reduction of Nitro Compounds.—The reduction of nitro compounds results in the formation of amido-compounds if carried out vigorously (e.g. with iron, zinc, tin, &c., and a suitable acid).   In this way nitrobenzene may be made to furnish amidobenzene or aniline, whilst meta-dinitrobenzene gives metadiamidobenzene (meta-phenylenediamine). If however the reduction of the latter compound be effected with a mild reducing agent such as ammonium sulphide in alcoholic solution, only one of the nitro groups is reduced and metanitraniline results.

When a nitro group is reduced it by no means follows that an amido-group is formed in its place ; two molecules may condense and in this way one may obtain the following series of compounds from nitro-benzene :

$$\text{Azoxybenzene} \quad C_6H_5 - N \overset{O}{\overset{\wedge}{-}} N - C_6H_5$$

$$\text{Azobenzene} \quad C_6H_5 - N = N - C_6H_5$$

$$\text{and} \quad \text{Hydrazobenzene} \quad C_6H_5 - NH - NH - C_6H_5$$
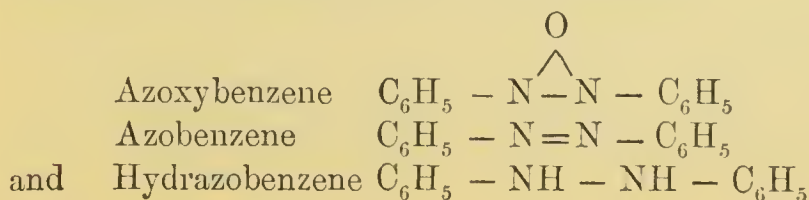
Besides these, two peculiar reduction processes have been observed within the last few years. Nitrobenzene when reduced by zinc dust in a neutral solution of calcium chloride furnishes β-phenylhydroxylamine, $C_6H_5 \cdot NHOH$ (Bamberger, Wohl). When gently oxidised, the phenyl-hydroxylamine is converted into nitroso-benzene, $C_6H_5 \cdot NO$. Gattermann has also observed that the passage of an electric current through nitrobenzene dissolved in concentrated sulphuric acid is accompanied with a simultaneous oxidation and reduction of the nitrobenzene, paramidophenol $C_6H_4(OH)(NH_2)$, results. This reaction has been proved in a great many cases, and has formed the subject of various patents.

30. **Preparation of Aniline.**—Weigh out 50 grams of nitrobenzene, 150 grams of granulated tin and 350 grams of commercial fuming hydrochloric acid. Place the tin and 100 grams of the hydrochloric acid in a round-bottomed flask of $1\frac{1}{2}$ to 2 litres capacity. Now raise the contents of the flask to boiling so that hydrogen begins to be evolved, remove the flame and connect the flask with a wide reflux condenser. Next add the nitro-benzene in small quantities at a time through the condenser : the reaction is apt to be very violent if large quantities are poured in. When about 15 grams of the nitro-benzene have been added, a second 100 grams of hydro-chloric acid are poured in, and then proceed with the addition of about 15 grams of the nitrobenzene also in small quantities. Add now the remainder of the hydro-chloric acid and the rest of the nitrobenzene. During the addition of the nitrobenzene be careful that the previous amount has been fully reduced before a fresh quantity is added. When the reaction is finished the smell of nitro-benzene should not be noticeable on removing the con-

denser from the flask.   The aniline must now be set free
from the hydrochloric acid with which it is combined ; this
may be effected by addition of caustic soda solution
(40–50 per cent.) or by means of the cheaper slaked lime.
In the latter case grind up 300–350 grams of slaked lime
with water to a thin paste and run it into the flask con-
taining the aniline and tin salt whilst the latter is still hot ;
take care, however, that no boiling takes place, or the
aniline will be taken away by the steam.   Test the contents
of the flask from time to time ; when a permanent alkaline
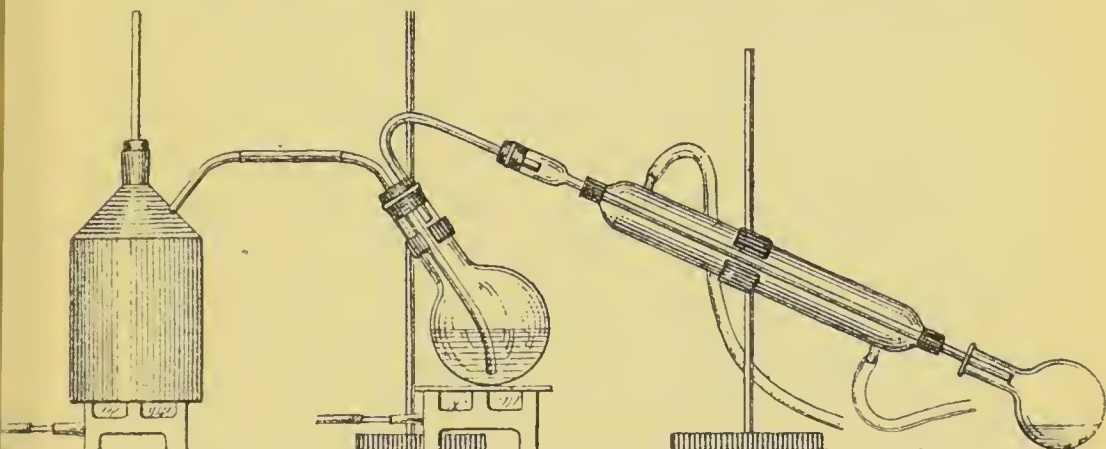
Fig. 60.

reaction has set in, the addition of the lime can be stopped.
Now connect up the flask with a steam-generating vessel on
the one hand and a condenser about 40 or 50 cm. in length on
the other.   The general arrangement of the apparatus is
shown in fig. 60.   The steam generator may be made of an
ordinary can of tin plate of the shape shown, to which a
side tube has been soldered.   The top is closed with a well-
fitting cork through which a safety tube passes.   The flask
containing the now alkaline mixture is supported by a
clamp in an inclined position, ' priming ' or blowing over of
liquid with the steam being avoided.   The inlet tube for

steam which is slightly curved should reach very nearly to the bottom of the flask so that any formation of a cake of solid matter at the bottom may be avoided. The exit tube leads to the condenser as shown. Both steam generator and flask are represented as being heated by Fletcher burners; Bunsen burners may of course be used. In this case support the generator on a tripod stand and the inclined flask on the ring of a retort stand; in any case protect the bottom of the flask from direct fire either by a sound piece of wire-gauze or by a piece of asbestos cardboard. Steam should be raised in the boiler whilst the neutralisation is proceeding; in this way one is able to pass the steam into the still hot solution, so that on the one hand a separation of solid matter is avoided, on the other no steam is required to raise the temperature of the contents of the flask. The flame under the flask should be regulated with care so as to avoid chances of cracking the flask. A steady current of steam is now blown through; the liquid running from the end of the condenser will have a milky appearance and separate into two layers in the receiver, a clear upper one consisting of a weak aqueous solution of aniline and a lower slightly yellow oily one of aniline. The distillation should be carried on until the distillate is coming over quite clear and has a scarcely perceptible smell of aniline.

Next separate the aniline from the supernatant water as completely as possible by means of a separating funnel; stand the separated aniline aside in a flask. To the aqueous portion add about 17 or 18 grams of common salt for each 100 c.cm. Shake up with ether, allow the ethereal solution of the rest of the aniline to collect on the top and separate it from the salt solution. Now add the ethereal solution to the remainder of the aniline and dry

the mixed aniline and ether with stick caustic potash. Pour
off the solution into a distilling flask, recover the ether by
distillation on the water-bath, using a long condenser for
the purpose ; when the ether is all over remove the con-
denser and replace it by a short cooling tube, and distil
the aniline with a naked flame.   Boiling point 182°.
About 33 grams of aniline should be obtained.

In cases where a large amount of a base such as aniline
are being prepared it is well to separate the distillate from
time to time, using the weak aqueous solution of aniline for
recharging the boiler and not submitting it to the some-
what expensive ether extraction process.

The reaction of the tin and hydrochloric acid on the
nitrobenzene may be expressed by the equation :

$$C_6H_5 \cdot NO_2 + 3Sn + 7HCl = C_6H_5 \cdot NH_2, HCl + 3SnCl_2 + 2H_2O.$$
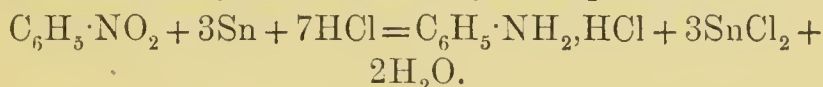
The reduction can be completed with less quantity of
tin, and in this case the stannous chloride produced acts
itself as a reducing agent, being thereby converted into the
stannic compound :

$$C_6H_5 \cdot NO_2 + 3SnCl_2 + 7\ HCl = C_6H_5 \cdot NH_2, HCl + 3SnCl_4 + 2H_2O.$$
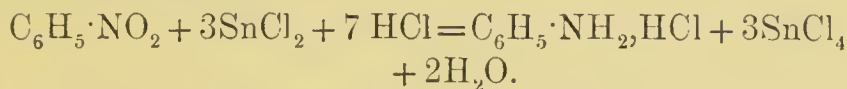
Sometimes an alkaline stannous compound is of use in
reducing a nitro to an amido compound. Stannous chloride
solution is first precipitated by the addition of sodium
hydroxide, but the stannous hydroxide is redissolved by an
excess of the reagent.   Roemer utilised such a solution to
reduce dinitroanthraquinone (1 : 5) to the corresponding
diamido-anthraquinone. The alkaline stannous solution
dissolves the dinitro compound with a greenish blue colour
(? intermediate product formed) ; on warming, the diamido-
anthraquinone is deposited in dark red needles.

31. **Preparation of Aniline Hydrochloride.**— Dissolve 2 grams of aniline in warm dilute hydrochloric acid ($2\frac{1}{2}$ c.cm. fuming acid to 15 c.cm. water). Pour the solution into an evaporating basin and evaporate gently on the water-bath until the salt begins to separate. Allow the solution to cool slowly, so that good crystals of the hydrochloride are obtained. Filter these off and dry on a porous tile.

Aniline forms fairly stable salts with acids. This salt-forming property may be weakened or destroyed by introduction of negative radicles in place of hydrogen—(a) into the NH_2-group, (b) into the benzene nucleus. Thus acetanilide or tribromaniline will not give hydrochlorides under the conditions of salt formation observed in this case.

Aniline and its salts may be recognised by the following tests :—

(a) Dissolve one or two drops of aniline in a few c.cm. of water. Then add drop by drop a bleaching powder solution. A purple colouration will be observed.

(b) Stir on a watch-glass one drop of aniline and five drops of concentrated sulphuric acid. Now add a drop of aqueous solution of potassium dichromate. A blue colouration will be produced, which however soon disappears.

(c) Warm four or five drops of aniline, about 2 c.cm. alcohol, and a piece of caustic potash about the size of a small pea in a test-tube. Now add a few drops of chloroform. An intolerable smell due to phenyl carbamine will be observed. This is formed according to the reaction :

$$C_6H_5 \cdot NH_2 + CHCl_3 + 3\ KOH = 3\ KCl + 3\ H_2O +$$
$$C_6H_5 \cdot N:C.$$
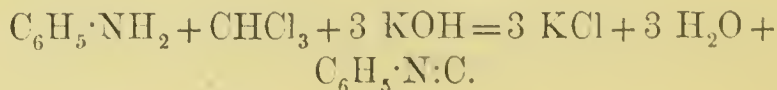
The following should also be tried. Add a few drops

of aniline to 1 c.cm. strong nitric acid. The mixture becomes hot ; on dilution with water a tarry mass separates and no crystalline nitraniline can be detected.

32. **Preparation of Acetanilide** $(C_6H_5 \cdot NH \cdot CO \cdot CH_3)$.—One hydrogen atom of the NH_2-group in aniline may be replaced by an acetyl group by the action of acetic anhydride, acetyl chloride or glacial acetic acid itself. Introduce into a flask of 300 c.cm. capacity 50 grams of aniline and 50 grams of glacial acetic acid. Fit the flask with a cork through which pass a reflux tube, 5 to 7 mm. interior diameter and about a metre in length (a reflux condenser is not necessary). Now heat the flask and its contents to boiling and keep it gently boiling for 12 hours. Then pour the contents of the flask into about a litre of cold water, filter off the acetanilide which separates in the solid condition, dissolve the acetanilide in as small a quantity of boiling distilled water as will take it all up, filter rapidly through a plaited filter and allow to cool slowly. The acetanilide separates out in large lustrous plates which are collected on a filter, washed with cold distilled water and dried. The mother liquor from the recrystallisation is not worth further working on account of the very sparing solubility of acetanilide in cold water. Melting point 112°. Yield about 50 grams.

When acetanilide (1 part) is dissolved in an excess of well-cooled fuming nitric acid (3 parts) a mixture of ortho and para acetnitranilides is formed. On pouring on to powdered ice the paranitranilide is precipitated, the ortho-compound can be extracted from the aqueous solution by shaking with chloroform. These two acetnitranilides may be hydrolysed by boiling with acids or alkalies, and the corresponding nitranilines obtained.

33. **Preparation of a Diphenylthiocarbamide**

$(CS(NHC_6H_5)_2)$ (Sulphocarbanilide).—When aniline is heated with carbon disulphide, hydrogen sulphide is evolved, and a derivative of sulphourea produced :

$$CS_2 + 2C_6H_5NH_2 = H_2S + CS(NHC_6H_5)_2.$$
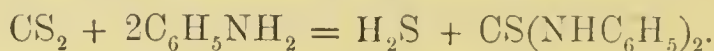
Mix in a flask of about 400 c.cm. capacity 50 grams each of aniline, carbon disulphide, and alcohol. Connect the flask with a reflux condenser, and heat the contents to gentle boiling for 12 hours. This operation must be carried out in the draught-chamber on account of the hydrogen sulphide evolved. At the end of the heating, pour the contents out into a large amount (say 2 litres) of water weakly acidified with hydrochloric acid. The sulphocarbanilide which now separates out is filtered off, washed with cold water and recrystallised from alcohol. Large colourless plates melting at 154° yield 40 to 50 grams.

The reaction may be carried out much more rapidly if caustic potash is added to the mixture ; the product is however not quite so clean. In the case of certain amines, it seems however impossible to work without the help of potash.

When diphenylthiourea is heated with hydrochloric acid it is broken up into aniline (which combines with the acid) and phenyl isothiocyanate :

$$CS(NHC_6H_5)_2 + HCl = C_6H_5NH_2,HCl + C_6H_5 \cdot N{:}C{:}S.$$
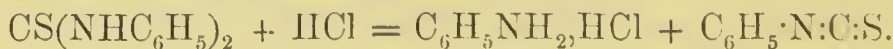
At the same time a small amount of triphenylguanidine is produced, owing to the interaction of the aniline and diphenylthiourea :

$$CS(NHC_6H_5)_2 + H_2N \cdot C_6H_5 = C({:}N \cdot C_6H_5)(NHC_6H_5)_2.$$
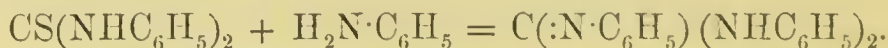
34. **Preparation of Phenyl-thiocarbimide** $(C_6H_5 \cdot N{:}C{:}S)$ (Phenyl Mustard Oil).—In a flask of 300–400 c.cm. capacity

put 30 grams of sulphocarbanilide and 100 c.cm. of fuming hydrochloric acid. Connect with a reflux condenser and boil for 40 minutes, by which time a brown oil will have separated out. Remove the flame, and disconnect the condenser, then fit the flask as in fig. 60, so that its contents may be distilled in steam. The phenyl mustard oil is carried over by this means as a nearly colourless oil, slightly heavier than water. Separate from the aqueous layer by means of a separating funnel, dry over calcium chloride and fractionate; the boiling-point is 220°.

The contents of the flask from which the phenyl mustard oil has been removed by steam distillation may now be worked up for the triphenylguanidine, which, as previously stated, also forms a product of the reaction. Transfer to a basin and evaporate on the water-bath until a glass rod dipped in the hot solution is covered with crystals on cooling. Then allow the contents of the basin to cool, filter off the triphenylguanidine hydrochloride which separates, wash with a small quantity of cold water, and decompose by boiling in a flask with a solution of caustic soda. The base is thus obtained free. Filter off, wash with water, and recrystallise from alcohol. White needles; melting point 143°.

Phenylthiocarbimide is a chemically active substance; it usually unites directly with primary bases forming derivatives of thiocarbamide. Thus, with ammonia it yields monophenylthiocarbamide ($NH_2 \cdot CS \cdot NHC_6H_5$). Pour three or four drops of the mustard oil into a test-tube, add about 1 c.cm. alcohol and three or four drops of aniline. Boil for a few minutes and then add hot water until a slight disturbance is seen in the liquid. Collect the plates which separate on cooling, press on a piece of porous earthenware, and when dry determine the melting-point.

They will be found to melt at 154°. The aniline and phenyl mustard oil have combined with formation of sulphocarbanilide :

$$C_6H_5 \cdot N{:}C{:}S + C_6H_5NH_2 = CS(NH \cdot C_6H_5)_2.$$

35. Preparation of Tribromaniline $(C_6H_2(NH_2)Br_3$. 1:2: 4:6).—Weigh out 13 grams of aniline into a flask of 400 c.cm. capacity and 80 grams (the theoretical quantity) of bromine into a beaker. Add the bromine very carefully, in small portions at a time, to the aniline; cooling the flask from the outside by holding it occasionally under running water. The addition of the bromine is accompanied by a somewhat energetic reaction. When the operation has proceeded so far that the contents of the flask become pasty, dilute with alcohol as occasion may require and proceed with the addition of the bromine. When all the latter has been added, cool the flask and its contents thoroughly, filter off the crystalline paste with the aid of the pump, wash with dilute alcohol, and lastly water and finally recrystallise from boiling strong alcohol. Long colourless needles; melting-point 116°. Yield nearly theoretical.

36. Preparation of Azoxybenzene $(C_6 \cdot H_5 \cdot N \overset{O}{\overset{\bigwedge}{-}} N \cdot C_6H_5)$.— Fit a flask of about 500 c.cm. capacity with a well-fitting cork and reflux condenser, and weigh into it 250 grams of dry methyl alcohol. Cut 10 grams of sodium into pieces about the size of a pea, and introduce these one by one into the methyl alcohol by dropping them down the condenser. The first few pieces of sodium should be introduced with care, as the reaction between the sodium and methyl alcohol—resulting in the formation of hydrogen and sodium methylate—will at first be somewhat violent;

afterwards the sodium can be introduced rather more rapidly. When all the sodium has been dissolved in the methyl alcohol, add 30 grams of nitrobenzene, and boil the contents of the flask gently for 6 hours on the water-bath. The sodium methylate will act as a reducing agent and the nitrobenzene be reduced to azoxybenzene:

$$4 \text{ } C_6H_5NO_2 + 3CH_3ONa = 2C_6H_5 - N\overset{O}{\overset{\wedge}{-}}N - C_6H_5 + 3 \text{ } H_2O + 3 \text{ } HCO_2Na.$$
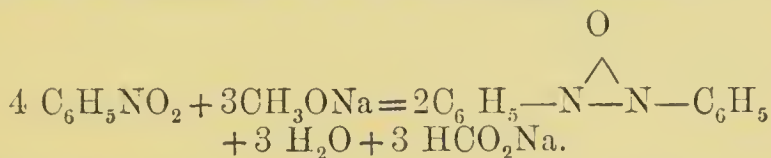
When the boiling under reflux has been finished, reverse the condenser, and distil off the excess of methyl alcohol; then wash the residue in the flask several times with water, the azoxybenzene being insoluble in this solvent.

Dissolve the residue of azoxybenzene in alcohol warmed to about 30°, filter the solution if necessary, add water to the solution until a slight disturbance is seen, then a drop or two of alcohol to remove this disturbance, and leave the solution in a crystallising dish to crystallise spontaneously. Collect the yellow needles which separate, wash with cold water and dry, first between filter paper and then over sulphuric acid. Melting-point 36°. Yield, about 22 grams.

37. **Preparation of Azobenzene** ($C_6H_5 \cdot N : N \cdot C_6H_5$).— Raise 200 c.cm. of methylated spirit to boiling-point in a flask provided with a reflux condenser, add 40 grams of powdered caustic soda and boil until the soda has been taken up into solution as far as possible. Then add 50 grams of nitrobenzene in small portions at a time to the boiling solution; this can be most readily done by inserting a funnel in the open end of the condenser. The whole mixture is warmed on the water-bath for 2 or 3 hours, by which means azoxybenzene is produced in the solution as given in the preceding preparation.

To effect the reduction of the azoxybenzene to azobenzene, 20 grams of zinc dust are added in small quantities at a time, best by raising the cork through which the condenser passes occasionally. The boiling under reflux must now be continued for another 10 or 12 hours, the flask being shaken occasionally. The condenser is then reversed, the alcohol distilled off (water-bath) as far as is practicable and warm water added to the residue. This precipitates not only azobenzene but also zinc hydroxide at the same time, the latter having been formed according to the equation :

$$C_6H_5 \cdot N \overset{O}{\overset{\triangle}{\frown}} N \cdot C_6H_5 + H_2O + Zn = C_6H_5 \cdot N : N \cdot C_6H_5 + Zn(OH)_2.$$
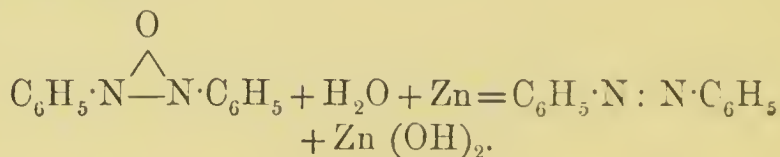
After filtering, extract the zinc hydroxide from the residue by dilute hydrochloric acid, wash with water, and recrystallise the residual azobenzene from hot alcohol. Large red plates. Melting-point 68°. Yield, about 40 grams.

38. **Preparation of Hydrazobenzene** ($C_6H_5 \cdot NH \cdot NH \cdot C_6H_5$). —Raise 100 grams of methylated spirit to boiling in an Erlenmeyer flask of 200–250 c.cm. capacity. Dissolve 30 grams of azobenzene in this alcohol; as soon as solution is complete add about 2 c.cm. of acetic acid and then zinc dust in small quantities at a time, keeping the contents of the flask boiling over a piece of wire gauze and shaking occasionally. The zinc dust acts as a reducing agent, and, as the alcohol contains a certain amount of water and a small amount of acetic acid has been added, the azobenzene is reduced in accordance with the equation :

$$C_6H_5 \cdot N:N \cdot C_6H_5 + 2H_2O + Zn = C_6H_5 \cdot NH \cdot NH \cdot C_6H_5 + Zn(OH)_2.$$
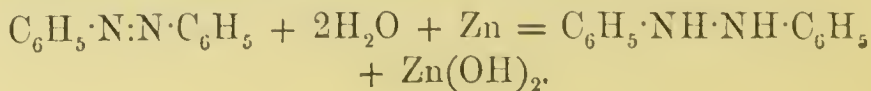
Some of the zinc naturally forms zinc acetate. When the red colour of the azobenzene has been entirely discharged and the solution is nearly colourless, filter rapidly through a plaited filter into a beaker and to the filtrate add boiling water to which some sulphurous acid has been added until a slight disturbance of the liquid takes place. Cover with a clock glass and allow to cool; the hydrazobenzene then separates out in colourless tablets. When cold, filter off the compound rapidly with the aid of the pump, wash with water containing sulphurous acid, and dry first between filter paper and then in a vacuum desiccator. The yield is nearly quantitative ; melting point 131°.

Other agents may be used for the reduction of azoben-zene, thus a cold alcoholic solution of azobenzene is de-colorised by passing in simultaneously currents of dry ammonia and hydrogen sulphide. In this case if a saturated solution of azobenzene be taken a great portion of the hydrazobenzene will crystallise out by itself since it is less soluble in alcohol than azobenzene.

It should be noted that the reduction is carried out in a neutral or alkaline solution ; if the solution be acid, the hydrazobenzene is changed into the isomeric benzidine which possesses more basic properties.

39. **Preparation of Benzidine** ($NH_2 \cdot C_6H_4 \cdot C_6H_4 \cdot NH_2$).— Hydrazobenzene when treated with mineral acids forms salts of the isomeric benzidine (diamidodiphenyl).

$$C_6H_5 \cdot NH \cdot NH \cdot C_6H_5 + 2HCl =$$
$$HCl, NH_2 \cdot C_6H_4 \cdot C_6H_4 \cdot NH_2, HCl.$$
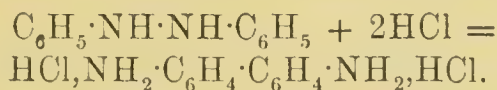
It is however unnecessary to first isolate hydrazobenzene and then to act on this with a mineral acid. The process of reduction and isomerisation can be carried out by one operation in the following manner. Dissolve 27 grams of

O

tin in 100 c.cm. of fuming hydrochloric acid by boiling
in an Erlenmeyer flask over wire gauze. Then dissolve
35 grams of azobenzene in 150 c.cm. of methylated spirit
contained in a flask of $\frac{1}{2}$ litre capacity, connected with a
reflux condenser and heated to boiling on a water bath.
Pour the hydrochloric acid solution of stannous chloride
gradually into the alcoholic azobenzene solution ; care must
be exercised, as the reaction is somewhat vigorous. During
the reduction some of the azobenzene is converted into
aniline ; the portion which goes first into hydrazobenzene
is partially converted into benzidine (the dipara-diamido
derivative of diphenyl), partially into diphenyline, an iso-
meric diamidodiphenyl (ortho-para derivative). The reac-
tion is soon finished, the condenser is then reversed and the
alcohol distilled off. To separate the benzidine from the
other basic products formed, dilute sulphuric acid is added
in excess to the contents of the flask. Benzidine sulphate
separates out, since it is nearly insoluble both in water and
alcohol. This is filtered off and washed with hydrochloric
acid until free from tin, after which the sulphuric acid is
removed from the base by grinding up in a mortar with a
slight excess of ammonia. After filtering off and washing
with a small quantity of cold water, the benzidine is re-
crystallised from a large quantity of boiling water. (About
$1\frac{1}{2}$ litres benzidine dissolves in 105 parts of boiling water,
but requires 2,500 parts of cold water for solution.) The
benzidine separates out on cooling in large colourless
leaflets which are filtered off, washed with small quantities
of distilled water on the pump and dried. Yield about
15 grams. Melting point 122°.

The filtrate from the benzidine sulphate should be
worked up for the contained diphenyline. The solution
is rendered alkaline by the addition of caustic soda and

is then shaken in a separating funnel with enough benzene to take up the separated bases. The aqueous solution is then carefully separated from the upper layer of benzene, which is washed once or twice by shaking with small quantities of water; the diphenyline is then removed from the benzene by agitation with dilute hydrochloric acid, aniline being naturally dissolved at the same time. The two bases are next removed from the benzene by shaking with repeated small quantities of dilute hydrochloric acid and the acid extract concentrated in a porcelain dish on the water bath. The benzene from which the bases have been extracted can be dried by fused calcium chloride and distilled. The hydrochloric acid solution deposits crystals of the hydrochloride of diphenyline when it has been concentrated sufficiently, the aniline hydrochloride remaining principally in the mother liquor. This crystallisation of the salt of the diamido base depends on its relatively sparing solubility in strong hydrochloric acid. The crystals are removed from the solution, the mother liquor being further concentrated to see if any more of the diphenyline hydrochloride separates.

The violet crystals may be purified and obtained in a colourless condition by solution in a small quantity of warm water and addition of an equal volume of fuming hydrochloric acid. Should it be desired to obtain the free base from this salt it may be dissolved in water, soda added and the base extracted with ether. The ethereal solution is then evaporated, the residue dissolved in warm alcohol (at about 40°–45°), the solution filtered if necessary, water added until a slight disturbance is occasioned and the diphenyline left to crystallise out. Colourless needles, melting point 45°. Yield about 6 grams.

In the case of azo-compounds in which one of the

para-positions to the azo group is already substituted, the benzidine change cannot take place. This matter has been very fully worked out recently by Jacobson and his pupils (Cf. *Liebig's Annalen* 1895, **287**, 97–220), who find that when paraethoxyazobenzene is reduced by stannous chloride in alcoholic solution, that the chief product is a derivative of ortho-phenylene diamine.

$$\langle \quad \rangle -N : N-\langle \quad \rangle OC_2H_5 + 2H = \langle \quad \rangle -NH-\langle \quad \rangle \begin{smallmatrix} OC_2H_5 \\ \\ NH_2 \end{smallmatrix}$$
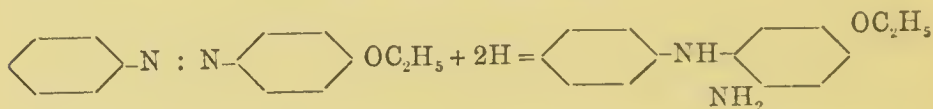
This change, in which one amido and one imido group are produced, has been named the ' semidine reaction,' and according to whether the amido group takes up the ortho or the para-position to the imido group, so the reaction is known as the ' ortho ' or ' para-semidine reaction.'

Section III.—Diazo-Compounds and Hydrazines

40. **Preparation of Diazobenzene Sulphate (Phenyldiazonium Sulphate), $C_6H_5 \cdot N_2 \cdot SO_4H$.**—Dissolve 15 grams of aniline in 150 grams of absolute alcohol (the alcohol must be at least of 95 per cent. strength) and add gradually 40 grams of concentrated sulphuric acid. The first addition of the acid causes a separation of aniline sulphate, which, however, goes into solution as more acid is added. The solution is then cooled by tap-water from the outside, until it has attained a temperature of about 15°. 20 grams of amyl nitrite are then gradually poured in, the liquid being constantly stirred. On leaving the mixture for 10 to 15 minutes at the ordinary temperature, it is usually found that a mass of needles, consisting of diazobenzene sulphate, has crystallised out ; should this not have happened, add a few drops of ether, which then brings

about the crystallisation. The diazobenzene sulphate should now be filtered off with the aid of the pump, and washed first with alcohol and then with ether. The alcoholic washings should not be added to the first filtrate; if, however, the ethereal washings be made up to about 75 c.cm. and added to the mother liquor, a fresh crystallisation of diazobenzene sulphate is brought about so that the yield is nearly quantitative. The salt may be dried at the ordinary temperature on a porous tile.

Heat a very small quantity of the salt in a test-tube, it will explode.

The reaction between the aniline, sulphuric acid and amyl nitrite can be expressed by the equation,

$$C_6H_5NH_2 + H_2SO_4 + C_5H_{11}{\cdot}O{\cdot}NO = C_6H_5{\cdot}N_2{\cdot}SO_4H$$
$$+ C_5H_{11}OH + H_2O.$$
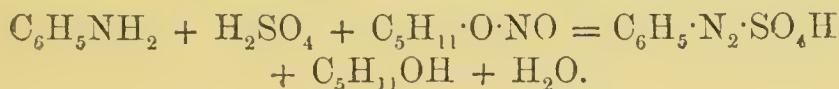
It is not necessary to first isolate the diazo-salt in the pure, dry condition when it is only desired to form the compound as an intermediate step in the preparation of some other substance. In this case it is customary to dissolve the base which is to be diazotised in the acid (either concentrated or dilute as circumstances may require), and after cooling to the neighbourhood of $0°$ C. to add the calculated quantity of sodium or potassium nitrite, dissolved in water. The mixture must be frequently agitated during the addition, so that escape of nitrous fumes does not take place. The reaction is then represented by the following equation, in which the nitrous acid is derived from the interaction of the excess of acid in which the amido-compound has been dissolved on the added nitrite:

$$C_6H_5NH_2,HCl + HNO_2 = C_6H_5{\cdot}N_2{\cdot}Cl + 2H_2O.$$
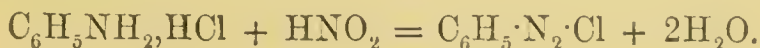
With regard to the structure of the diazo-group, the customary way has been to represent the constitution of diazobenzene chloride by the formula $C_6H_5 \cdot N : N \cdot Cl$. Blomstrand[1] many years ago proposed, however, the

$$C_6H_5 \cdot \overset{\overset{\textstyle N}{\textstyle |||}}{N} \cdot Cl$$

alternative formula $C_6H_5 \cdot \overset{\overset{N}{|||}}{N} \cdot Cl$.   Since, however, diazobenzene chloride readily reacts with phenols to form substances of the general type $C_6\dot{H}_5 \cdot N : N \cdot C_6H_4 \cdot OH$, and by reduction furnishes phenylhydrazine hydrochloride, $C_6H_5 \cdot NH \cdot NH_2, HCl$, Blomstrand's formula was generally disregarded.   His formula has, however, been recently brought again under notice, and from a study of the physical properties of diazo-solutions, it seems very probable that the compounds with acids really contain

the phenyldiazonium group $C_6H_5 \cdot \overset{\overset{N}{|||}}{N}-$

Besides the phenyldiazonium salts, true diazo-compounds of the type $C_6H_5 \cdot N : N - R$ are known to exist; these can apparently assume two forms.   According to Bamberger the two forms are to be regarded as structurally different; Hantzsch is, however, of the opinion that in addition to diazonium compounds both syn-diazo and anti-diazo compounds exist.   These stereoisomeric forms might then be represented by the general formulæ,

$$\begin{array}{cc} C_6H_5-N & \qquad C_6H_5-N \\ \parallel & \qquad\qquad \parallel \\ X-N & \qquad\quad N-X. \\ \text{Syn-diazo} & \qquad \text{Anti-diazo} \end{array}$$
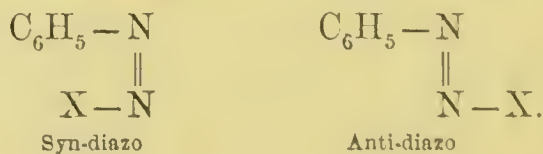
[1] *Berichte*, 1875, **8**, 51.   Cf. *Journ. prakt. Chem.* 1896, **54**, 305.

ELIMINATION OF THE DIAZO-GROUP

41. Preparation of Phenol (C_6H_5OH) from Diazobenzene Sulphate.—Since the diazobenzene sulphate will only decompose if kept, it had better be immediately worked up for another preparation. If the solution of a diazo-salt in water be boiled, the corresponding hydroxy-compound is formed whilst nitrogen escapes :

$$C_6H_5 \cdot N_2 \cdot SO_4H + H_2O = C_6H_5 \cdot OH + N_2 + H_2SO_4.$$
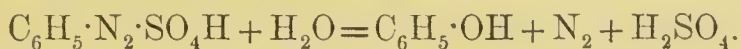
This reaction is analogous to what happens when nitrous acid acts on a primary amine of the fatty series. Thus ethylamine and nitrous acid give ethyl alcohol, water and nitrogen without an intermediate diazo-compound being formed.

Dissolve the diazobenzene sulphate in water and boil the solution for about 20 minutes in a flask provided with a reflux tube. Nitrogen is rapidly evolved. When the decomposition is complete, arrange apparatus so that steam can be blown through the liquid, and collect the distillate until only a negligible quantity of phenol is carried over by the steam. Saturate the distillate with common salt, and extract the phenol from the solution by means of ether. Dry the ethereal extract with quicklime, and then submit it to fractional distillation. Ether passes over at first, afterwards phenol ; boiling point $184°$.

42. Conversion of Aniline into Benzene.—Dissolve 37 grams of aniline in 80 grams of fuming hydrochloric acid which has previously been diluted with 120 c.cm. of water, warming if necessary for the purpose of getting all the aniline hydrochloride into solution. Cool down to the ordinary temperature, and to the solution, which should be in a flask of about 400 c.cm. capacity, add 200 grams of ice

broken into small pieces.   The solution of aniline hydro-
chloride is now diazotised by adding to it a second solution
made by dissolving 30 grams of sodium nitrite (96 per cent.)
in 40 grams of water; the addition of the latter should take
place in such a way that only small quantities are added
at a time, and after every fresh addition of the nitrite
solution the contents of the flask are well agitated and no
more of the nitrite is poured in until the smell of nitrous
acid has disappeared.   As soon as the smell of nitrous acid
becomes permanent, or free nitrous acid can be detected
by potassium iodide and starch, cease the addition of the
sodium nitrite, all the aniline hydrochloride having been
converted into diazobenzene chloride.

To effect the reduction of the diazobenzene chloride to
benzene, an alkaline stannous solution is employed; the two
following solutions should therefore be prepared before the
diazotisation is carried out.   Stir up 100 grams of crys-
tallised stannous chloride with 120 grams of water, and pour
the solution (which will probably be milky owing to separa-
tion of basic chloride) into 80 grams of caustic soda dis-
solved in its own weight of water.   The addition must be
carefully made, with continued stirring and avoidance of rise
of temperature, otherwise much of the tin will separate out
as black crystalline stannous oxide.   The other solution
required is made by dissolving 40 grams of caustic soda in
60 grams of water; add 50 grams of ice to this solution, and
pour into it in a slow stream the solution of diazobenzene
chloride, stirring continually.   The alkaline diazo-solution
prepared in this way is now poured into the solution of
sodium stannite, which should be at a temperature of about
15°, and contained in a flask provided with a reflux con-
denser. Nitrogen will be evolved, and a layer of benzene
will gradually collect on the top of the solution.   As soon

as the evolution of nitrogen has ceased, heat the flask and
its contents for a few minutes on the water-bath; cool down;
transfer the contents of the flask to a separating funnel;
separate the alkaline stannic solution from the benzene;
wash the latter two or three times with water; dry the ben-
zene with not too great a quantity of stick caustic potash;
and distil from a small fractionating bulb. Colourless
liquid, boiling point 80°·5. Yield nearly theoretical.

The reactions which take place may be expressed by
the following equations :

$$C_6H_5 \cdot N_2 \cdot Cl + NaOH = NaCl + C_6H_5 \cdot N : N \cdot OH.$$
$$C_6H_5 \cdot N : N \cdot OH + Sn(ONa)_2 = C_6H_6 + N_2 + SnO(ONa)_2.$$
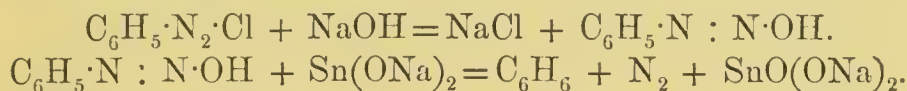
This method of replacing an amido-group by hydrogen
by first diazotising the amido-compound and then reducing
with an alkaline stannous solution is due to Friedländer
(*Ber.* 1889, **22**, 587). Griess had previously devised a
method which consisted in boiling a diazo-salt with alcohol,
e.g :

$$C_6H_5 \cdot N_2 \cdot SO_4H + C_2H_5OH = C_6H_6 + H_2SO_4 + H_2O$$
$$+ CH_3 \cdot CHO.$$
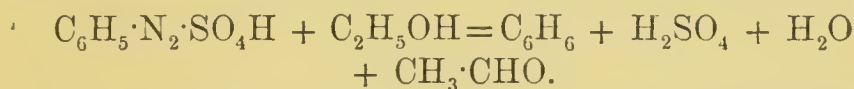
In this case the alcohol acts as the reducing agent,
being itself oxidised to aldehyde. The method has, however,
a great drawback, viz. that in the case of the higher
homologues of aniline, the diazo-compounds react with the
alcohol in a quite different manner, ethers of the corre-
sponding phenols being obtained :

$$C_6H_3(CH_3)_2 \cdot N_2 \cdot SO_4H + C_2H_5OH = C_6H_3(CH_3)_2 \cdot O \cdot C_2H_5$$
$$+ H_2SO_4.$$
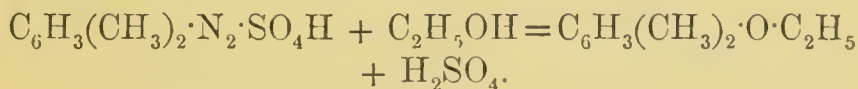
Another method of replacing amido-groups by hydrogen
atoms consists in the reduction of the diazo-compound to

the corresponding hydrazine, and oxidising the latter with ferric chloride.

REPLACEMENT OF AMIDO-GROUPS BY HALOGENS

The amido-groups of aromatic bases may be replaced by fluorine, chlorine, bromine, iodine, and also cyanogen by first preparing a diazo-salt and then treating this in a suitable manner. For instance, simple boiling with the corresponding concentrated hydracid usually effects a certain amount of conversion into a halogen derivative, but at the same time some of the corresponding phenol is usually obtained. Thus on boiling a solution of diazobenzene chloride with strong hydrochloric acid the following reactions take place :

$$C_6H_5 \cdot N_2 \cdot Cl = C_6H_5Cl + N_2.$$
$$C_6H_5 \cdot N_2 \cdot Cl + H_2O = C_6H_5OH + N_2 + HCl.$$
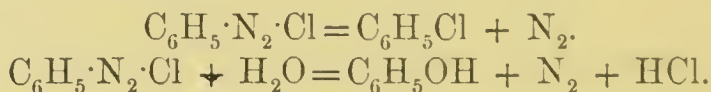
The yield of halogen derivative may be much increased by the adoption of Sandmeyer's method.

43. **Conversion of Aniline into Chlorbenzene** (C_6H_5Cl).— Sandmeyer's method for replacing the amido-group by a halogen atom depends on the formation of a diazo-salt, and the reaction of this with the corresponding cuprous halogen compound. A cuprous-diazo double salt is first formed, which decomposes smoothly when warmed into nitrogen, the halogen derivative of the hydrocarbon and cuprous halogen compound. We can represent the change which takes place by the following equations in the case of diazobenzene chloride and cuprous chloride :

$$C_6H_5 \cdot N_2 \cdot Cl + Cu_2Cl_2 = C_6H_5 \cdot N_2 \cdot Cl,Cu_2Cl_2.$$
$$C_6H_5 \cdot N_2 \cdot Cl,Cu_2Cl_2 = C_6H_5Cl + N_2 + Cu_2Cl_2.$$
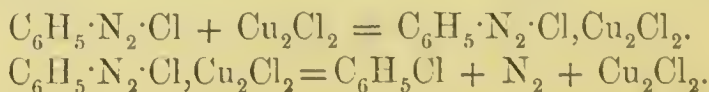
In carrying out the reaction, the cuprous chloride solution

must be first prepared. A solution of about ten per cent. strength can be prepared by boiling together in a flask $12\frac{1}{2}$ grams of crystallised copper sulphate and 6 grams of sodium chloride with 25 c.cm. water. After boiling some time, 50 grams of concentrated hydrochloric acid are added and 7 grams of copper turnings or filings, and the boiling is then continued until the solution is decolorised. In this way a solution of cuprous chloride in excess of strong hydrochloric acid is obtained, more of the latter being added, so that the total weight is made up to 100 grams. This solution is then transferred to a flask provided with a reflux condenser; meanwhile a solution of diazobenzene chloride is prepared.

Dissolve 20 grams of aniline in 45 grams of concentrated hydrochloric acid which has been diluted with 150 grams of water, and keeping the liquid cool, diazotise by the addition of 16 grams of sodium nitrite dissolved in 40 grams of water. The cuprous solution is now raised to about 50° and the diazo-solution poured in gradually, the flask and its contents being meanwhile thoroughly agitated. Each addition of the solution causes at first the separation of a yellow precipitate of the double cuprous-diazo chloride, which, however, decomposes almost immediately with evolution of nitrogen and separation of chlorbenzene. When the conversion is complete, the flask is arranged for steam distillation and the chlorbenzene driven over in a current of steam. The distillate separates into two layers: an upper layer of water, whilst the heavier chlorbenzene sinks to the bottom of the receiving flask and is separated from the water by a separating funnel. After drying over calcium chloride, it is distilled, boiling point 132°. Colourless liquid, specific gravity 1·12837 at 0° (Adrieenz). Yield nearly theoretical.

Brombenzene may be similarly prepared, a solution of cuprous bromide being used instead of the cuprous chloride employed in the preparation of chlorbenzene.

44. **Preparation of Iodbenzene** (C_6H_5I).—Dissolve 9·3 grams of aniline in a mixture of 20 grams of concentrated sulphuric acid and 80 grams of water. Cool the mixture by the addition of pieces of ice, and diazotise by the gradual addition of 7·5 grams of sodium nitrite dissolved in 10 grams of water. When the diazotisation is complete, pour the solution into 18 grams of potassium iodide dissolved in 40 grams of water, and contained in a small flask. The mixed solutions when warmed on the water-bath evolve nitrogen, whilst iodbenzene separates out as a heavy oil. The reaction may be represented by the equation,

$$C_6H_5 \cdot N_2 \cdot SO_4H + KI = C_6H_5I + KHSO_4 + N_2.$$
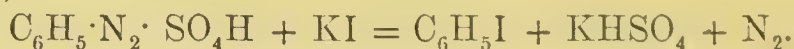
Blow over the iodbenzene in a current of steam; separate from the water which passes over at the same time; dry over calcium chloride; and distil. Colourless liquid, boiling point 188°, specific gravity 1·833 at 15°.

We note in this preparation that free hydriodic acid (*i.e.* acidified solution of potassium iodide) is sufficient to effect the replacement of the diazo-group by iodine, and that there is no necessity to employ a cuprous salt.

45. **Preparation of Benzonitrile** (C_6H_5CN).—The amido-group present in aniline may also be replaced by cyanogen by means of the diazo-reaction. Prepare cuprous cyanide by dissolving 70 grams of crystallised copper sulphate in 300 c.cm. of water and adding to it 80 grams of 90 per cent. potassium cyanide dissolved also in 300 c.cm. of water. This must be done in a well ventilated draught cupboard, as cyanogen is evolved, and consequently risks

of poisoning must be avoided. The flask is connected
with a reflux condenser, and heated so that its contents
are raised nearly to boiling ; a solution of diazobenzene
chloride is then introduced.   Prepare the diazo-solution
from 20 grams of aniline, dissolved in 45 grams of hydro-
chloric acid (sp. gr. 1·19) and 150 grams of water, cooling
as in previous cases and diazotising with 16 grams of
sodium nitrite dissolved in 40 grams of water. On mixing
the solutions, reaction sets in and benzonitrile is formed ;
as this is but very slightly heavier than water, cool when
the reaction is finished and extract with ether.   Dry the
ethereal extract with calcium chloride, and submit to frac-
tional distillation.   The benzonitrile passes over at 191°
as a colourless liquid.

46. **Preparation of Phenylhydrazine** ($C_6H_5 \cdot NH \cdot NH_2$).
The aromatic hydrazines are prepared by the reduction
of the corresponding diazonium salts.   Formerly this was
effected by means of alkaline sulphites ; now more
frequently by Victor Meyer and Lecco's method with
stannous chloride :

$$C_6H_5 \cdot N_2Cl + 2SnCl_2 + 4HCl = 2SnCl_4 +$$
$$C_6H_5 \cdot NH \cdot NH_2, \, HCl.$$
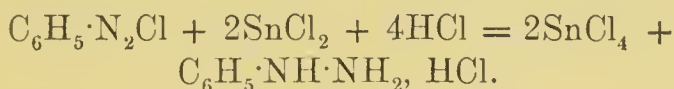
Weigh out 28 grams of aniline into a mortar and 420
grams of fuming commercial hydrochloric acid into a
beaker.   Add the hydrochloric acid to the aniline in small
quantities at a time, stirring up the mixture, which
becomes very hot, with the pestle.   When all the aniline
appears to have been neutralised by the acid, grind the
cake of aniline hydrochloride to a paste with more of the
acid, taking care that no lumps are left, and then rinse it
completely with more of the acid into a flask of 1½-litre
capacity.   Cool this mixture of finely divided aniline

hydrochloride and hydrochloric acid by placing the flask in a freezing-mixture made with ice and salt; when the mixture shows a temperature of 0° C., diazotisation may be begun by the addition of a solution of 22 grams of 95 per cent. sodium nitrite in 30 c.cm. water. The addition of the sodium nitrite must take place in small quantities at a time, the liquid being well agitated after each addition and replaced in the freezing-mixture. The temperature during the diazotisation should not rise above 5°.[1]

During the process of diazotisation a stannous solution should be prepared by dissolving 120 grams of crystallised stannous chloride in 120 grams of fuming hydrochloric acid. The stannous chloride used should be of good quality; if so it will dissolve almost without residue in the quantity of hydrochloric acid stated, the temperature being very much lowered by the addition of the salt. This solution should now be kept cool by means of a freezing-mixture until it is required.

Meanwhile, the diazotisation is continued, the sodium nitrite being added until free nitrous acid can be detected in the solution. The diazotised solution and the solution of stannous chloride are now both carefully cooled to 0° C., the latter then being added to the former in small quantities at a time; the contents of the flask are well agitated after each addition, and care is taken that the temperature does not rise too far. The contents of the flask, which consist of a colourless paste of minute crystals of phenylhydrazine hydrochloride, are now allowed to stand a few minutes, and then collected by the aid of the

[1] This, and similar diazotisations can be readily carried out with the help of a mechanical stirrer; in this case the salt solution to be diazotised is placed in a beaker surrounded by a freezing-mixture, and the nitrite solution allowed to flow in drop by drop from a stoppered funnel.

filter-pump and a Buchner funnel.   The mass is pressed down as thoroughly as possible in the funnel; washed a few times with concentrated hydrochloric acid; pressed down on porous earthenware to remove as much free acid as possible; and then dissolved in the smallest possible quantity of water.   Phenylhydrazine hydrochloride is easily soluble in water, though nearly insoluble in concentrated hydrochloric acid.

The solution of the salt is transferred to a fairly capacious separating funnel, and strong caustic soda solution ($33\frac{1}{3}$ per cent.) poured in, until the tin precipitate is redissolved by excess of the alkali.   The phenylhydrazine which partially separates is extracted completely from the solution by shaking with ether; the ethereal solution is then separated, dried completely over anhydrous potassium carbonate, and submitted to fractional distillation.   When the last of the ether has been distilled off (the greater part should be removed by the water-bath), the thermometer rapidly rises to about 200°, and all that comes over after this temperature up to 240° is collected.   Since a certain amount of ammonia is always formed in this first distillation, and dissolves in the distillate, this should be purified by leaving it for some days over sulphuric acid in a vacuum. The liquid is then again rectified, the portion distilling between 225° and 240° being collected apart.   Yield 20–23 grams.

Pale yellow oil or crystals of melting point 23°, boiling point 233°–234°.   The substance soon assumes a much darker colour on exposure to the air.

Cover 4 grams of phenylhydrazine with concentrated hydrochloric acid.   The liquid sets to a colourless crystalline mass; dry this by pressing it on porous earthenware.

Dissolve 1 gram of the salt so obtained in 10 c.cm.

water in a test-tube. Add 1 gram of benzaldehyde drop by drop, and then add a solution of sodium acetate in excess. Shake thoroughly ; a yellow precipitate of benzal-phenylhydrazone will be obtained :

$$C_6H_5 \cdot NH \cdot NH_2 + C_6H_5 \cdot CHO$$
$$= H_2O + C_6H_5 \cdot CH : N \cdot NH \cdot C_6H_5.$$
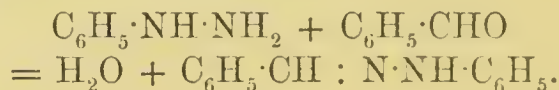
Collect the precipitate, wash once or twice with cold water, and recrystallise from alcohol. On cooling the benzal-phenylhydrazone will be deposited in pale yellow needles of melting point 152°·5.

Phenylhydrazine reacts very readily in this manner with almost all aldehydes and ketones, water being elimi-nated and a phenylhydrazone formed. When warmed with a solution of glucose (or fructose), three molecules of the hydrazine react with one molecule of the sugar. One molecule of the hydrazine oxidises the $CH(OH)$ group next to the aldehyde group to ketonic carbonyl, being itself reduced to aniline and ammonia. Both the ketonic and aldehydic carbonyls react with the other two molecules of phenylhydrazine, phenylglucosazone, $C_{18}H_{22}N_4O_4$, being formed according to the equation,

$$
\begin{array}{l}
CH_2 \cdot OH \\
| \\
CH \cdot OH \\
| \\
CH \cdot OH \\
| \\
CH \cdot OH \; + \; 3C_6H_5 \cdot NH \cdot NH_2 \; = \\
| \\
CH \cdot OH \\
| \\
CHO
\end{array}
\qquad
\begin{array}{l}
CH_2 \cdot OH \\
| \\
CH \cdot OH \\
| \\
CH \cdot OH \\
| \\
CH \cdot OH \; + \; C_6H_5NH_2 \; + \; NH_3 \; + \; 2H_2O \\
| \\
C : N \cdot NH \cdot C_6H_5 \\
| \\
CH : N \cdot NH \cdot C_6H_5.
\end{array}
$$
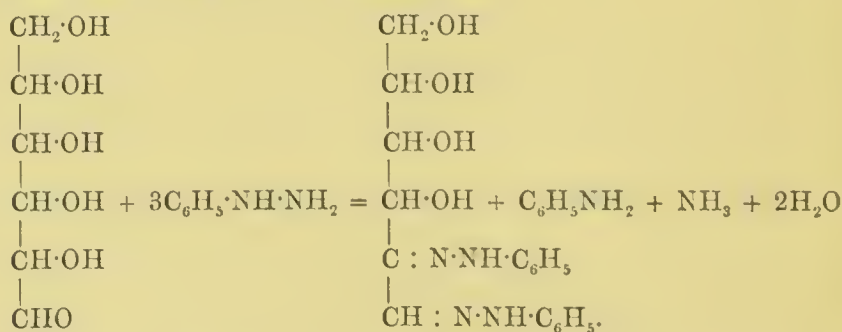
Dissolve 1 gram of phenylhydrazine hydrochloride in 10 c.cm. water, and to this add 1½ gram of crystallised sodium acetate. Pour the solution so obtained into 2 c.cm.

water containing ·6 gram of glucose in solution. Warm
the mixture in the water-bath, continuing the heating as
long as a yellow precipitate forms. Now allow the solution
to cool ; collect the precipitate which has been obtained ;
wash with cold water ; and recrystallise from alcohol.
Small yellow crystals, melting point 144°–145°.

Phenylhydrazine containing an NH_2 group shows many
reactions of the primary amines. We may, for instance,
prepare from it a large series of urea derivatives.

Dissolve 1 gram of phenylhydrazine hydrochloride in
5 c.cm. of water, and add to the solution ·5 gram of
potassium cyanate dissolved in about 2 c.cm. of water. A
white crystalline precipitate of phenylsemicarbazide is
immediately obtained ; collect and recrystallise from boiling
water. Colourless leaflets melting at 172°.

The compound has resulted according to the equation,

$$C_6H_5 \cdot NH \cdot NH_2, HCl + KCNO$$
$$= KCl + C_6H_5 \cdot NH \cdot NH \cdot CO \cdot NH_2.$$
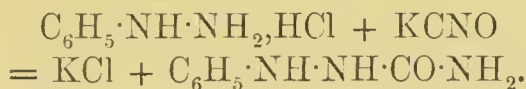
Dissolve a few drops of phenylhydrazine in ether, add
an equal number of drops of phenyl mustard oil, and stand
the solution aside. Soon pale yellow prisms of diphenyl-
thio-semicarbazide separate out ; these melt at 177°. The
formation of this compound may be represented by the
equation,

$$C_6H_5 \cdot NH \cdot NH_2 + C_6H_5N : C : S = CS{<}^{NH \cdot NH \cdot C_6H_5}_{NH \cdot C_6H_5.}$$

Add a drop or two of phenylhydrazine to 1 c.cm. of Fehl-
ing's solution in a test-tube. The Fehling's solution is
reduced even in the cold, cuprous oxide being precipitated ;
whilst aniline and benzene are formed and nitrogen evolved.
Primary hydrazines when boiled with a solution of copper

sulphate are converted principally into the corresponding hydrocarbon :

$$C_6H_5 \cdot NH \cdot NH_2 + 2CuSO_4 + H_2O$$
$$= C_6H_6 + N_2 + 2H_2SO_4 + Cu_2O.$$
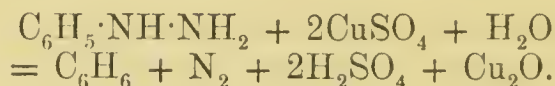
Section IV.—Sulphonation

The aromatic hydrocarbons may be more or less readily sulphonated by treatment with sulphuric acid. This may take place according to circumstances either when the compounds are allowed to react on one another at ordinary temperatures or are heated together. Generally speaking, the sulphonation can be effected more easily by employing fuming sulphuric acid (which we may look upon as a solution of sulphur trioxide in hydrogen sulphate), or by chlorsulphonic acid. Not only can hydrogen atoms in hydrocarbons be replaced by SO_3H groups, but the reaction may be extended to the derivatives of these, this being especially easy to carry out in the case of the amido- and hydroxy-compounds.

47. **Preparation of Sodium β-Naphthalene Sulphonate** $(\beta\text{-}C_{10}H_7SO_3Na)$.—Naphthalene yields with concentrated sulphuric acid a- and β-naphthalene sulphonic acids, according to the temperature at which the reaction is carried out :

$$C_{10}H_8 + H_2SO_4 = C_{10}H_7SO_3H + H_2O.$$
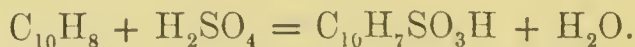
By heating four parts of naphthalene with three parts of concentrated sulphuric acid for eight to ten hours at a temperature not above 80°, a mixture of the two acids is obtained, which are separated by the different solubility of their lead salts, the β-salt being the less soluble in water (and alcohol). At a higher temperature the β-acid is

formed almost exclusively; in fact if *ā*-naphthalene-sulphonic acid is heated with strong sulphuric acid to a moderately high temperature, it is almost entirely converted into the *β*-acid.   The *β*-acid can therefore be easily prepared by the employment of a higher temperature.

Heat a mixture of 100 grams of naphthalene and 100 grams of concentrated sulphuric acid in a flask for ten hours at 160°, an oil-bath being used to attain this temperature.   At the end of this time allow the mixture to cool to about 80°, and carefully pour into 1 litre of boiling water.   After a thorough stirring, allow to cool, and if an upper layer has been formed, remove this and use the aqueous lower layer.   Heat this in a large evaporating basin, adding calcium carbonate in small portions at a time, and stirring thoroughly after each addition.   As soon as the liquid is saturated with the chalk (no evolution of carbon dioxide on adding a fresh quantity), filter hot, boil the residual calcium sulphate several times with water, filtering hot each time, and evaporate down the united filtrates to a small bulk in an evaporating dish until the salt begins to separate.   On cooling, calcium *β*-naphthalene sulphonate will crystallise out ; separate this from the mother liquor by means of the pump, wash once or twice with cold water in small quantities, and dry the salt completely at 120°.

A specimen of the salt may be kept ; convert the major portion, however, into the corresponding sodium salt, as this will be required in a subsequent preparation.   For every 100 grams of calcium salt to be converted, weigh out 23·4 grams of pure anhydrous sodium carbonate. Dissolve the calcium naphthalene-sulphonate in boiling water, and to the boiling solution add a fairly concentrated

solution of the sodium carbonate.   Boil for a few minutes, then allow to subside, and filter off the precipitate of calcium carbonate from the solution of sodium naphthalene sulphonate.   Concentrate this solution to a small bulk, and crystallise out the sodium salt.

48. **Preparation of Sulphanilic Acid (Paraamidobenzene Sulphonic Acid,** $C_6H_4{<}{NH_2 \atop SO_3H}$).—Weigh out into a flask (about 250 c.cm. capacity) 90 grams of concentrated sulphuric acid.   Add to this 30 grams of aniline, pouring the latter in in small quantities at a time, and shaking after each addition so as to obtain a uniform mixture. Now heat the flask and its contents to 180°–190° by means of an oil-bath, and after four hours take out a small specimen of the melt by means of a glass rod.   Treat this in a test-tube with dilute caustic soda solution in which it should entirely dissolve.   If this is the case, warm the solution, and if no odour of free aniline is detected, the reaction between the aniline and sulphuric acid may be taken as finished.   Should the presence of unsulphonated aniline be detected, the heating of the contents of the flask in the oil-bath must of course be continued until aniline is no longer to be detected.   Then pour the contents of the flask into about 1 litre of cold water; the sulphanilic acid separates out as a somewhat coloured crystalline powder. Filter this off by means of the pump, and recrystallise from boiling water, decolorising the solution by means of animal charcoal if necessary.

Sulphanilic acid forms colourless prismatic crystals containing two molecules of water of crystallisation; these are, however, soon lost on exposure to the air.   From the amount of aniline taken about 32 grams of crystallised sulphanilic acid should be obtained.

The sulphonation of the aniline took place according to the equation,

$$C_6H_5NH_2 + H_2SO_4 = C_6H_4 \begin{cases} (1) \ NH_2 \\ (4) \ SO_3H \end{cases} + H_2O.$$
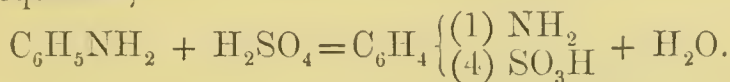
Section V.—Phenols

The phenols are the hydroxyl derivatives of the aromatic hydrocarbons. Many of them occur in coal tar, *e.g.* phenol (carbolic acid) C_6H_5OH, cresols $C_6H_4(CH_3)OH$, &c. The phenols may be obtained from the aromatic hydrocarbons in a variety of ways.

1. Friedel and Crafts found that if aluminium chloride were dissolved in a boiling hydrocarbon and a stream of oxygen led in, that a phenol was produced :

$$C_6H_6 + O = C_6H_5OH.$$
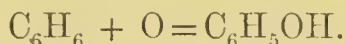
2. The hydrocarbon may be sulphonated and the resulting sulphonic acid fused with caustic potash or soda. Thus the sodium derivative of β-naphthol is obtained by fusing sodium β-naphthalene sulphonate with excess of caustic soda :

$$C_{10}H_7SO_3Na + 2NaOH = Na_2SO_3 + C_{10}H_7ONa + H_2O.$$
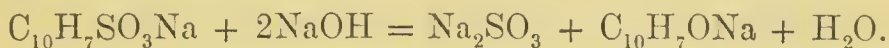
3. The hydrocarbon may be nitrated, the resulting nitro-substance reduced to an amido-derivative, the latter treated with nitrous acid (*see* preparation 41).

4. Many homologues of phenol can be prepared by heating phenol with fatty alcohols and zinc chloride; thus isobutyl phenol from isobutyl alcohol and phenol (Liebmann) :

$$C_6H_5OH + C_4H_9OH = C_4H_9 \cdot C_6H_4 \cdot OH + H_2O.$$
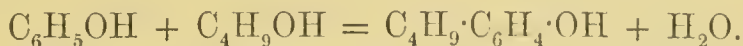
5. Hydroxy acids split off carbon dioxide when heated with baryta :

$$C_6H_4 \begin{cases} OH \\ CO_2H \end{cases} + BaO = BaCO_3 + C_6H_5OH.$$
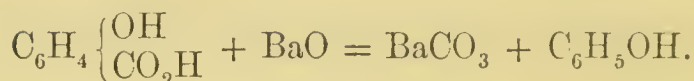
In the above methods of preparation it will be noted that no method of preparation analogous to the replacement of halogen by hydroxyl in the fatty series is described. The chlorine in chlorbenzene is too firmly united to the rest of the molecule to allow of such a replacement. The chlorine atom is weakened in its attachment to the molecule if a negative group be introduced into either the ortho- or para-position. Thus, when ortho- or para-chlornitrobenzene are heated with soda solution to $130°$, the chlorine atom is eliminated, and the sodium salt of ortho- or para-nitrophenol produced :

$$C_6H_4 \begin{cases} Cl \\ NO_2 \end{cases} + 2\ NaOH = C_6H_4 \begin{cases} ONa \\ NO_2 \end{cases} + NaCl + H_2O.$$
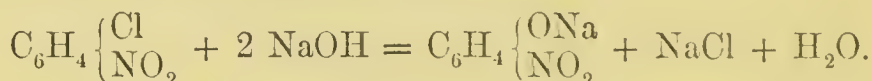
With an increase in the number of negative groups this behaviour becomes so marked that symmetrical trinitrochlorbenzene (picryl chloride, $C_6H_2Cl(NO_2)_3$ $(1:2:4:6)$ behaves like an acid chloride.

The phenols readily form substitution derivatives. Phenol and bromine in aqueous solution give a white precipitate of symmetrical tribromphenol, $C_6H_2(OH)Br_3$ $(1:2:4:6)$. With dilute nitric acid phenol yields a mixture of the ortho- and para-nitro substitution products ; more energetic nitration results in the formation of dinitrophenol, $C_6H_3(OH)(NO_2)_2$, whilst when the phenol is first sulphonated by warming with concentrated sulphuric acid and then nitrated with strong acid, picric acid, $C_6H_2(OH)(NO_2)_3$, results, the sulphonic group being eliminated.

Esters of the phenols may be prepared ; for the preparation of acetates, acetyl chloride or acetic anhydride are

employed. In the latter case the phenol in question is boiled under reflux with acetic anhydride, fused sodium acetate being also frequently added (Liebermann's method). The melt resulting from the reaction is then usually boiled for some time with water to effect the decomposition of the excess of acetic anhydride.

In benzoylating phenols, direct heating with benzoyl chloride is sometimes resorted to ; more frequently the phenol is dissolved in dilute sodium hydrate solution, containing as many molecules of soda as correspond to the hydroxyl groups present in the phenol ; the calculated quantity of benzoyl chloride is then added, and the mixture well agitated. The reaction may be represented generally by the equation :—

$$R(OH)_n + nNaOH + nC_6H_5COCl = nNaCl + nH_2O + R(O \cdot COC_6H_5)_n.$$
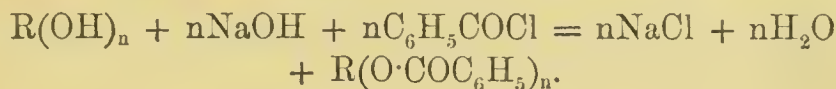
A similar method may be used for preparing benzene sulphonates. (Use benzenesulphonyl chloride.)

49. **Preparation of β-Naphthol.**—β-naphthol is prepared from sodium β-naphthalenesulphonate by fusion with caustic soda. Such a fusion cannot be carried out in glass or porcelain vessels ; a copper crucible or small cast-iron saucepan should be used on the small scale, and the thermometer used for noting the temperature must be protected from the action of the alkali by a copper or iron sheathing. Enamelled vessels are generally useless, since most of the enamels are made to resist the action of acids and not of alkalies, by which they are frequently rapidly destroyed at a high temperature.

The thermometer and its casing are shown in fig. 61. Cut a piece of narrow wrought-iron tubing, of such a length that when the bulb of the thermometer is within a

short distance of the one end of the tubing, the 230° mark
on the scale is just clear of the other end.   The iron
tubing for this purpose should have an internal diameter
but little greater than the external diameter of the thermo-
meter.   Close one end A of this iron tube by hammering
the iron, finally welding the closure so that
it shall be impermeable to the melted soda.
Place a small quantity of somewhat finely
crumbled asbestos at this end of the tube to
protect the bulb of the thermometer from
scratching, and then introduce the latter into
the tube, fixing it firmly in place by passing
it through a cork at B.   The cork B should
have a small slit cut in it to allow for the
expansion of the air within the tube.   Enclose
the upper end of the tube with a cork C ;
this is to serve as a handle, so that on
stirring the melt with the tube and ther-
mometer one may avoid burning one's hand.
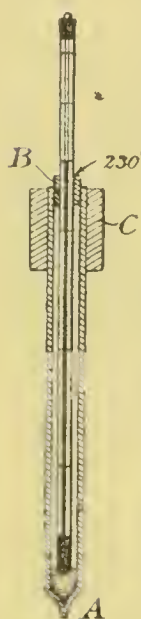
Melt together in a small stout cast-iron sauce-
pan 200 grams of caustic soda with 25 grams of
water, and continue the heating with a strong flame until
the thermometer and its tube which are used as a stirrer
show a temperature of 280°.[1]   Now add 70 grams of
sodium β-naphthalene-sulphonate (dried thoroughly at 110°–
120°) in small quantities at a time, so that the temperature
of the melt does not fall to any great extent, otherwise
the mass will become too viscous to stir.   When all the
sodium salt has been added, gradually raise the tempera-
ture ; about 300° steam begins to come off, and the
viscid mass is rather difficult to stir.   Soon the mass
becomes of a thinner consistency and darker colour, and

FIG. 61

_____
[1] The eyes should be protected during this operation.

separates into two layers. Remove the thermometer tube from the melt, allow the latter to cool; when cold remove from the saucepan, and mechanically separate the upper layer of sodium naphtholate from the lower layer of excess of caustic soda. Dissolve the former in hot water, and add to the hot solution a mixture of equal parts by weight of commercial strong hydrochloric acid and water, until the liquid has a distinctly acid reaction. Allow the mixture to cool, filter off the precipitated β-naphthol, wash with cold water, and carefully dry. Finally purify the β-naphthol by distillation (b. p. 285°–290°). The distilling flask should have only a short side tube, which passes through a cork into a wider cooling tube, so as to avoid stoppage owing to solidification of the distillate. Melting point 122°. Yield about 35 grams.

50. **Preparation of β-Naphthyl Benzoate** (β-$C_{10}H_7 \cdot O \cdot COC_6H_5$).—Dissolve 1·25 gram of caustic soda in 50 c.cm. water contained in a small bottle provided with a well-fitting cork. Now add 3 grams of β-naphthol, and, corking the bottle, agitate thoroughly until the β-naphthol is dissolved. Then add 3 grams of benzoyl chloride to the contents of the bottle, and shake thoroughly until the smell of benzoyl chloride has practically disappeared. The reaction which takes place between the sodium β-naphtholate and benzoyl chloride may be represented by the equation:—

$$C_{10}H_7ONa + C_6H_5COCl = NaCl + C_{10}H_7 \cdot O \cdot COC_6H_5.$$
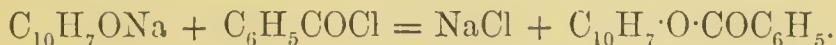
Filter off the precipitate of β-naphthyl benzoate, wash with cold water, and recrystallise from alcohol. Small colourless needles, m.p. 107°. Yield 3 to 4 grams.

51. **Preparation of Ortho- and Para-nitrophenols.** $\left(C_6H_4 \begin{Bmatrix} OH \\ NO_2 \end{Bmatrix} \right)$.—As previously mentioned, phenol when

nitrated with dilute nitric acid yields a mixture, of the ortho- and para-mononitro substitution derivatives :

$$C_6H_5OH + HNO_3 = C_6H_4 \begin{cases} OH \\ NO_2 \end{cases} + H_2O.$$
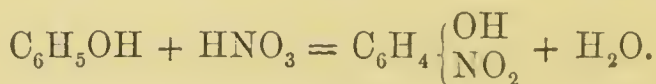
These may be separated by means of steam distillation, the ortho-compound being volatile under these circumstances, the para-compound remaining in the distilling flask.

For the nitration 5 parts of nitric acid of sp. gr. 1·13 are needed for every part of phenol. Supposing that 80 grams of phenol are to be nitrated, 400 grams of such a dilute acid will be required. The requisite quantity of this may be obtained by mixing 124 grams of nitric acid of sp. gr. 1·42 (*i.e.* 87$\frac{1}{3}$ c.cm.) with 276 c.cm. of water. Having this nitric acid in a flask of about one-litre capacity, add 80 grams of phenol in small quantities at a time, shaking the contents of the flask well after each addition. The addition of the phenol causes a strong discoloration of the acid, so that by the time all the phenol has been added the liquid has become of a very dark brown colour, whilst a nearly black oil has collected at the bottom of the flask. The mixture is now allowed to stand at the ordinary temperature overnight, and next morning the acid liquid is carefully decanted off, and the residue washed by decantation several times with water to remove free nitric acid. About 200 c.cm. of water are now poured on to the residue, which is then subjected to steam distillation (*see* fig. 60). The distillation is carried on as long as the liquid which distils over has a yellow colour ; in the receiving flask, water and a heavier yellow crystalline solid will be collected, the latter consisting of pure orthonitrophenol. Care has to be exercised that the orthonitrophenol does not solidify in the Liebig's condenser and so stop it ; when the liquid is found

to begin to solidify there, turn off the condensing water until it is again melted out. Should the distillate of orthonitrophenol be required in larger crystals and not in semi-fused masses, it may be recrystallised from hot water ; it then forms yellow prisms of melting point 45°.

The paranitrophenol contained in the flask in which the steam distillation has been carried out is mixed with a large amount of tarry matter, the separation of which causes some trouble, especially when due care has not been exercised during the nitration in the first instance. Boil the residue with hot concentrated hydrochloric acid ; allow the hot liquid to stand for a few minutes, so that the tarry matter may settle ; pour off the hot solution into a beaker (not, however, filtering the solution, since the hydrochloric acid will break the filter paper) ; and allow the paranitrophenol to crystallise out. The substance so obtained will form somewhat dirty coloured needles ; recrystallise it from boiling water, using animal charcoal to effect complete decolorisation. Paranitrophenol forms colourless needles or prisms, melting point 115°.

Section VI.—Aromatic Acids

The acids of the aromatic series exhibit considerable analogy to those of the fatty series, and are prepared frequently by similar synthetical process. One can, however, frequently prepare them by the energetic oxidation of hydrocarbons, which, in addition to a benzene nucleus, have fatty side chains, the latter being oxidised to carboxyl groups, whilst the nucleus, unless hydrogen atoms have been substituted by hydroxyl or amido groups, shows a great resistance to oxidation.

The ortho-dicarboxylic acids of the aromatic series

furnish internal anhydrides with ease ; this corresponds to the formation of anhydrides from succinic, maleïc and citraconic acids.   Meta- and para-dicarboxylic acids do not, however, form such internal anhydrides ; we therefore have nothing in the aromatic series to correspond to the conversion of glutaric acid into glutaric anhydride.

The aromatic hydroxy acids are frequently obtained from the sodium derivatives of phenols by the action of carbon dioxide at a somewhat elevated temperature ; this will be illustrated by the synthesis of salicylic acid.

52. **Preparation of Benzonitrile** ($C_6H_5 \cdot CN$).

This substance can be prepared in various ways, $e.g.$ the dehydration of ammonium benzoate or benzamide, distillation of the salts of benzene-sulphonic acid with cyanides, and the distillation of benzoic acid with thiocyanates. The latter method will be described here, potassium thiocyanate being employed.   Half the benzoic acid is thereby converted into potassium benzoate :

$$C_6H_5 \cdot COOH + KCNS = HCNS + C_6H_5 \cdot COOK,$$

the liberated thiocyanic acid reacting with the remainder of the benzoic acid, according to the equation,

$$C_6H_5 \cdot COOH + HCNS = C_6H_5 \cdot CN + H_2S + CO_2.$$
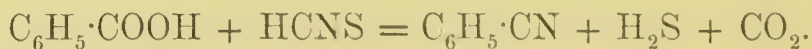
Obviously two molecules of benzoic acid must be taken for each molecule of thiocyanate ; the excess of benzoic acid can, however, be easily recovered from the potassium salt.

Heat in an oil-bath to 150° a flask containing a mixture of 76 grams of benzoic acid and 30 grams of potassium thiocyanate.   The flask should be provided with a cork and reflux tube about 70 cm. in length and of 1 cm. internal diameter.   Continue the heating, gradually raising the temperature to 190°, until the contents of the flask

set to a solid mass; this should be carried out in the draught cupboard on account of the sulphuretted hydrogen evolved. Allow the oil-bath to cool sufficiently; remove the reflux tube, and replace it with a bent tube and condenser; and raising the temperature of the bath, and occasionally warming the neck of the flask, distil off the benzonitrile which has been produced. The liquid distillate so obtained contains small quantities of benzoic acid; transfer it, therefore, to a separating funnel; agitate with dilute ammonia solution; separate the benzonitrile as completely as possible from the upper aqueous solution; and fractionally distil the product. Benzonitrile is a colourless liquid of sp. gr. 1·023 at 0°; it smells like bitter almonds, and boils at 191°.

The potassium benzoate remaining in the flask from which the benzonitrile has been distilled should be extracted with hot water, the solution filtered, and hydrochloric acid added. On cooling the benzoic acid crystallises out.

53. **Preparation of Benzyl Chloride** ($C_6H_5 \cdot CH_2Cl$).

In accordance with what has been said with regard to the oxidation of aromatic hydrocarbons having side chains, toluene may be directly oxidised to benzoic acid by boiling with dilute nitric acid, the reaction following the equation,

$$C_6H_5 \cdot CH_3 + 3O = C_6H_5 \cdot COOH + H_2O.$$
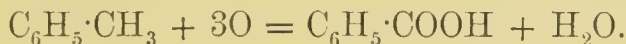
This reaction does not give very good results in practice; it is better to first replace hydrogen atoms of the methyl group with chlorine. This can be done by chlorinating toluene at a boiling temperature in bright daylight; direct sunshine is even better. In this way one obtains successively benzyl chloride, $C_6H_5CH_2Cl$, benzal chloride, $C_6H_5 \cdot CHCl_2$, and benzotrichloride, $C_6H_5 \cdot CCl_3$. By hydrolysis, these three chlorine substitution products are con-

verted into benzyl alcohol, $C_6H_5 \cdot CH_2OH$, benzaldehyde, $C_6H_5 \cdot CHO$, and benzoic acid, $C_6H_5 \cdot COOH$ respectively. The first two substances may, however, be also converted into benzoic acid if the hydrolysis be performed in presence of an oxidising agent. The preparation of benzyl chloride will therefore be first described, and the subsequent conversion of this into benzoic acid by long boiling with dilute nitric acid then taken.

Fit up a chlorine apparatus capable of giving at least 100 to 150 grams of chlorine, either employing manganese dioxide and strong commercial hydrochloric acid, or a Kipp's apparatus for the purpose. Provide this apparatus with a drying bottle containing strong sulphuric acid, and make a connection from this to a flask of about 300 c.cm. capacity, in which 100 grams of toluene have been weighed out. The toluene must have a boiling point of 111°; be careful that benzene and xylenes are not contained in it. The flask, together with the toluene, is weighed; through the cork not only the leading tube to pass the chlorine into the toluene is fitted, but also a reflux condenser to return the vapour of the boiling toluene to the flask. The apparatus must be fitted up near a window so that the reaction can take place in as bright daylight as possible. As this will very likely mean that the operation cannot be performed in a draught cupboard, the upper end of the reflux condenser should be connected with tubing to lead away the hydrogen chloride which is evolved in considerable quantity during the chlorination process according to the equation,

$$C_6H_5 \cdot CH_3 + Cl_2 = C_6H_5 \cdot CH_2Cl + HCl.$$
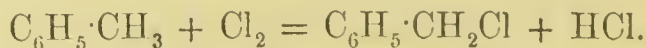
Heat the toluene contained in the flask to boiling, and lead in a steady and somewhat strong stream of chlorine,

disconnecting the apparatus occasionally in order to measure the increase in weight of the contents of the flask. When this weight increase is 37 to 38 grams stop the reaction, transfer the liquid to a suitably sized flask (preferably round-bottomed), fit this with a column (Wurtz's) and thermometer, and submit the liquid to fractional distillation. During this process a small amount of unacted-on toluene will be first obtained; then comes the second fraction, which may be collected between 155° and 190°. This fraction is the largest, and contains practically the whole of the benzyl chloride; what comes over above 190° consists principally of benzal chloride (b. p. 206°) and benzotrichloride (b. p. 213°–214°).

Rectify the second fraction (which should weigh more than 100 grams), and collect what comes over between 176° and 181° as practically pure benzyl chloride; the quantity obtained should be about equal to the weight of toluene taken, 70–75 per cent. of the theoretical yield.

Benzyl chloride is a colourless liquid of penetrating odour, specific gravity 1·107 at 14°.

54. **Preparation of Benzoic Acid** ($C_6H_5 \cdot COOH$).

Benzoic acid can be prepared on the small scale from benzyl chloride by the method of Lunge and Petri, which consists in boiling the substance for some time with dilute nitric acid :

$$C_6H_5 \cdot CH_2Cl + O_2 = C_6H_5 \cdot COOH + HCl.$$
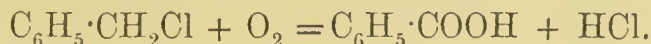
Make up 250 grams of dilute nitric acid, containing 30 per cent. of HNO_3. This corresponds to a specific gravity of 1·185 (22·5° Bé. or 37° Tw.) ; for the quantity of dilute acid required, 108 grams of nitric acid of specific gravity 1·42, or 134 grams if the specific gravity be 1·35, will be necessary. Pour this acid into a flask of 500 600 c.cm.

capacity; add 50 grams of benzyl chloride; connect the flask with a reflux condenser; and raise the contents to boiling. After about ten hours' boiling the smell both of benzyl chloride and benzaldehyde should have entirely disappeared; if so, allow the liquid to cool, the benzoic acid finally solidifying. Collect this on a filter; wash two or three times with cold water; dissolve the acid in hot dilute ammonia; filter the solution if necessary from any undissolved matter; acidify with dilute hydrochloric acid, allow to cool; collect the precipitated benzoic acid on a filter; wash once or twice with cold water; and finally either recrystallise the acid from a large quantity of boiling water (one part of benzoic acid requires about 18 parts of water at $100°$ for solution), or else dry the acid and submit it to sublimation.

Benzoic acid forms colourless shining needles or leaflets, melting point $121·4°$.

55. **Preparation of Benzoyl Chloride** (C_6H_5COCl).

This substance may be prepared by the action of the chlorides of phosphorus upon benzoic acid; thus with phosphorus trichloride we have the following equation,

$$3C_6H_5COOH + PCl_3 = H_3PO_3 + 3C_6H_5COCl.$$
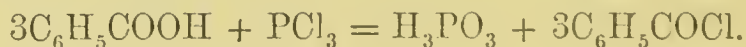
Secondary reactions, however, take place, and hydrogen chloride is evolved in considerable quantity. Benzoyl chloride may also be prepared by the interaction of phosphoryl chloride and sodium benzoate.

Melt 65 grams of benzoic acid in a porcelain dish, allow the melted acid to cool, and break it up into small pieces. Transfer 60 grams of this acid to a round-bottomed flask of 200 c.cm. capacity; provide this with a well-fitting cork and long reflux condenser; and then pour on to the benzoic acid 36 grams of phosphorus trichloride. Heat the flask

and its contents very gradually by means of a sulphuric acid bath; hydrogen chloride soon begins to make its escape; the reaction should therefore be carried out in a draught cupboard. About 100° the contents of the flask get really liquid; the heating is still continued until 120° is attained, and this temperature is then maintained for about four hours. The contents of the flask are now allowed to cool, the liquid poured off as completely as possible from the residue in the flask into a distilling flask, and submitted to distillation. Exercise great care as to the transference of the liquid to the distilling flask and its subsequent distillation, since benzoyl chloride attacks the eyes and throat in a most unpleasant manner. Collect the liquid which passes over between 193° and 203° in a second distilling flask, from which in turn the second fractionation can be made. Benzoyl chloride will thus be obtained as a colourless liquid of boiling point 198° and specific gravity 1·2122 at 20°.

It should be received during this second fractionation in tubes, which can easily be sealed off, and have been previously weighed. Not only is the liquid unpleasant when exposed to the air, but is gradually converted by moisture into benzoic acid. This causes the glass stoppers of bottles containing the liquid to become firmly fixed; whilst corked bottles are impossible, owing to the action of the benzoyl chloride on the cork.

56. **Preparation of Benzamide** ($C_6H_5CONH_2$).—Benzamide may be obtained by a variety of processes; for the various methods of preparation of amides refer to the subject of fatty amides on p. 128. In this case we shall deal with the action of ammonia on an acid chloride, the ammonia being conveniently employed in the form of ammonium carbonate:

$$C_6H_5 \cdot COCl + (NH_4)_2CO_3 = C_6H_5 \cdot CO \cdot NH_2 + NH_4Cl$$
$$+ H_2O + CO_2.$$
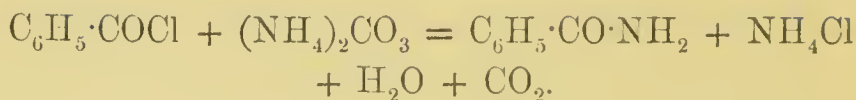
Grind up in a mortar to a fine powder 12 grams of commercial solid ammonium carbonate; this is really a mixture of acid ammonium carbonate and ammonium carbamate; its composition is empirically represented by the formula $N_3H_{11}C_2O_5$. Add to the finely powdered salt 10 grams of benzoyl chloride in small quantities at a time, and continue the grinding until the smell of the benzoyl chloride has entirely disappeared. The ammonium chloride which has been formed may be separated from the benzamide by the greater solubility of the former in cold water. Wash the mass, therefore, two or three times, using but small quantities of cold water on each occasion. The residue containing the greater portion of the benzamide is then dissolved in a sufficient quantity of boiling water and filtered hot. On cooling the benzamide separates out in colourless monoclinic tablets, melting point 128°.

57. **Preparation of Ethyl Benzoate** ($C_6H_5COOC_2H_5$).— Ethyl benzoate can be prepared from benzoic acid by the usual methods. The esterification of the acid may most easily be brought about by the action of anhydrous hydrogen chloride or sulphate on benzoic acid dissolved in absolute alcohol.

Introduce into a flask of about 300 c.cm. capacity 50 grams of benzoic acid, 100 grams of absolute alcohol, and 10 grams of concentrated sulphuric acid. Connect the flask with a reflux condenser, and boil the contents of the flask gently (water-bath) for three hours. Then distil off the greater part of the alcohol with the help of the water-bath, pour the residue in the flask into $\frac{1}{2}$ litre of water, and add solid sodium carbonate until the liquid has a neutral

reaction. The ethyl benzoate which has separated as an oil slightly heavier than water is next extracted with ether in a stoppered funnel, and the ethereal solution separated from the aqueous solution of sodium sulphate and benzoate. Transfer the ethereal solution to a small flask; dry it thoroughly with ignited potassium carbonate; transfer to a distilling flask, and after driving off the ether with the aid of the water-bath, rectify the ethyl benzoate with the naked flame. Ethyl benzoate is thus obtained as a colourless liquid boiling at 213°; the amount of ester obtained should be about equal to the weight of benzoic acid employed.

58. **Preparation of Salicylic Acid** $\left(C_6H_4 \begin{cases} (1)\ OH \\ (2)\ COOH \end{cases} \right)$.

In salicylic acid we have to deal with a compound which is both a carboxylic acid and a phenol at the same time. The acid occurs in nature, possibly in the free state in the flowers of *Spirea ulmaria*, and certainly as the methyl ester, $C_6H_4 \begin{cases} (1)\ OH \\ (2)\ COOCH_3 \end{cases}$, in oil of wintergreen (*Gaultheria procumbens*). From this ester it may be obtained by hydrolysis; it is, however, usually prepared synthetically by the action of carbon dioxide on heated sodium phenolate (Kolbe's process). The reaction takes place in two stages, which we can represent by one equation in the following manner:—

$$C_6H_5ONa + CO_2 = C_6H_5 \cdot O \cdot CO_2Na = C_6H_4 \begin{cases} OH \\ CO_2Na. \end{cases}$$
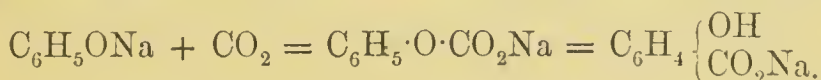
The sodium salicylate reacts, however, with sodium phenolate to form the basic sodium salicylate; half the phenol employed is therefore recovered in an unchanged condition:

$$C_6H_4 \begin{cases} OH \\ CO_2Na \end{cases} + C_6H_5ONa = C_6H_4 \begin{cases} ONa \\ CO_2\,Na \end{cases} + C_6H_5OH.$$
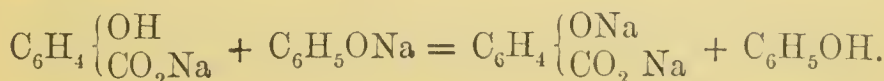
Dissolve 21 grams of powdered 96 per cent. caustic soda in an equal weight of water, and add gradually to this solution 47 grams of phenol. Evaporate down the solution so obtained in an iron dish, stirring continually so as to avoid any decomposition of the sodium phenolate, and finally dry the mass so obtained very thoroughly in the air-oven at 150°–160°. Finally powder the sodium phenolate, dry again, and transfer it to a dry flask of about 300 c.cm. capacity, which must be tightly corked until ready for use.

Meanwhile a Kipp for generating carbon dioxide is prepared, connected with a washing bottle containing
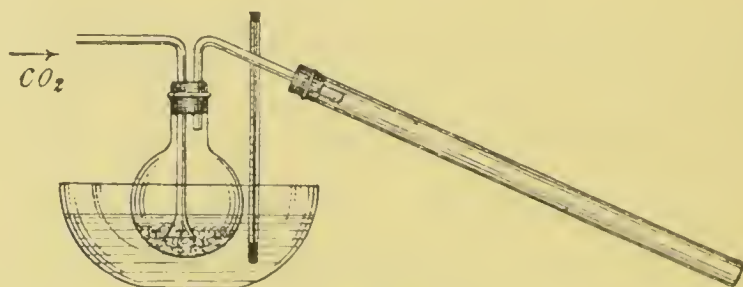
Fig. 62.

strong sulphuric acid, and the tube leading from this passed through a cork, which fits the flask containing the sodium phenolate tightly. The carbon dioxide leading tube must pass nearly to the bottom of the sodium phenolate; to avoid all risk of stoppage the end of the tube should be slightly enlarged. The cork carrying this tube, and fitting the flask in which heating is to take place, is also provided with an elbow tube to allow of the circulation of the carbon dioxide and the removal of the phenol which distils off; this elbow tube passes at its other end into a wider tube, which serves for the condensation

and recovery of the phenol. The flask containing the well-dried sodium phenolate is now attached to the rest of the apparatus just described (*see* fig. 16), the air inside the apparatus displaced by carbon dioxide, and the flask containing the sodium phenolate heated by means of an oil-bath to 180°. After some time, the current of carbon dioxide being steadily maintained at a slow rate, phenol begins to distil over. The quantity of phenol obtained afterwards becomes somewhat greater; the temperature is then raised to 200°, and kept at this point until no more phenol comes over. After the mass in the flask has cooled down sufficiently, it is dissolved in hot water, the solution filtered, and a small amount of hydrochloric acid added to precipitate tarry matters, which are always formed in the course of this reaction. These are then separated by filtration, the salicylic acid precipitated in the cold by a further quantity of hydrochloric acid, filtered off and re-crystallised from boiling water, animal charcoal being used to effect complete decolorisation.

Salicylic acid forms fine colourless needles, which melt at 155°–156°; it requires about thirteen times its weight of water at 100° and about 450 parts at 15° to effect its solution. The aqueous solutions of its salts are coloured a deep violet on addition of ferric chloride. It sublimes when gradually heated; rapid heating brings about a partial decomposition into phenol and carbon dioxide.

59. **Preparation of Phthalic Acid** $\left(C_6H_4\begin{Bmatrix}(1)\ COOH\\(2)\ COOH\end{Bmatrix}\right)$.

Phthalic acid may be obtained by the oxidation of naphthalene with nitric acid :

$$C_6H_4\begin{cases}CH=CH\\ \quad |\\ CH=CH\end{cases} + 9O = C_6H_4\begin{cases}COOH\\COOH\end{cases} + 2CO_2 + H_2O.$$
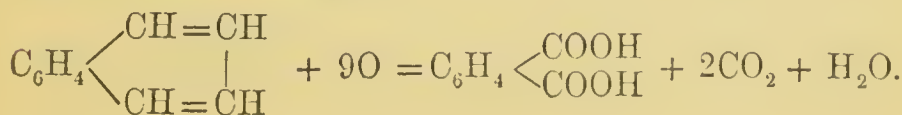
It is, however, better to first convert the naphthalene into naphthalene tetrachloride, $C_{10}H_8Cl_4$, and to then oxidise this with nitric acid.   Grind 80 grams of potassium chlorate to a fine powder and mix intimately with 40 grams of finely powdered naphthalene.   Add this mixture in small quantities to 400 grams of commercial fuming hydrochloric acid.   Remove the naphthalene tetrachloride, which separates as a yellowish pasty mass, from the hydrochloric acid, rinse it several times with water, press on filter paper, and wash with ligroin.   Now boil the naphthalene tetrachloride with 400 grams of nitric acid (250 grams of sp. gr. 1·42 and 150 grams of sp. gr. 1·5) in a flask provided with a reflux tube.   Do not add all the nitric acid at once, but in successive portions of 100 grams, so as to avoid too violent a reaction.   When all the substance has gone into solution, distil off the nitric acid from a retort, using considerable caution.   When the liquid has been concentrated to a small bulk, pour the contents of the retort into a beaker, and recrystallise the phthalic acid from boiling water.

Colourless rhombic crystals ; 100 parts of water dissolve ·54 of the acid at 14°, but 18 parts at 99°.   The melting point varies with the state of aggregation of the acid, since on heating it readily loses water and passes over into phthalic anhydride.

$$C_6H_4{\displaystyle <}^{COOH}_{COOH} = H_2O + C_6H_4{\displaystyle <}^{CO}_{CO}{\displaystyle >}O.$$
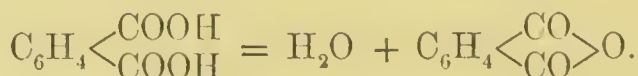
Should phthalic anhydride be desired instead of the acid, distil the latter from a small retort, the neck of which passes into a fairly wide condensing tube.   The anhydride will thus be obtained as long colourless needles melting at 128° and boiling at 276°.

60. **Preparation of Cinnamic Acid from Benzaldehyde** ($C_6H_5 \cdot CH : CH \cdot COOH$).—Mix together in a small flask 20 grams of benzaldehyde and 30 grams of acetic anhydride. Add, with continual shaking, 10 grams of fused and finely powdered sodium acetate, taking care that this does not form a hard cake at the bottom of the flask. Provide the flask with a well-fitting cork and reflux tube or condenser, and after carefully warming the flask and its contents, keep the latter gently boiling for eight hours. Now add 150 c.cm. of boiling water, arrange the flask and its contents for steam distillation, and blow steam through as long as the distillate smells of benzaldehyde. Then make the contents of the flask alkaline by the addition of powdered sodium carbonate ; in this way the cinnamic acid will pass into solution. Filter the hot liquid, add hydrochloric acid, and allow the liquid to cool. Separate the acid from the mother liquor by filtration, wash it once or twice with small quantities of cold water, and finally recrystallise it from boiling water. It will thus be obtained as colourless needles of melting point 133°. With the quantities taken, the yield will be about 12 grams.

In this reaction condensation is effected between the sodium acetate and the benzaldehyde, the acetic anhydride acting as a dehydrating agent :

$$C_6H_5 \cdot CHO + CH_3 \cdot COONa = C_6H_5 \cdot CH : CH \cdot COONa + H_2O.$$
$$H_2O + (CH_3 \cdot CO)_2O = 2CH_3 \cdot COOH.$$
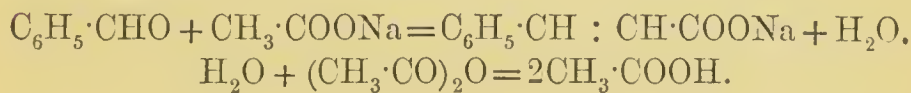
If, in this reaction, salicylaldehyde be substituted for the benzaldehyde, the corresponding orthohydroxycinnamic acid is not obtained. The acetyl derivative of this compound appears to be first formed. It loses, however, the

elements of acetic acid, and passes over into an internal
anhydride of orthohydroxycinnamic acid (cumarin).

$$C_6H_4\!\!\begin{array}{c}OCO{\cdot}CH_3 \\ CH:CH{\cdot}COOH\end{array} = CH_3{\cdot}COOH + C_6H_4\!\!\begin{array}{c}O - CO \\ | \\ CH = CH\end{array}.$$
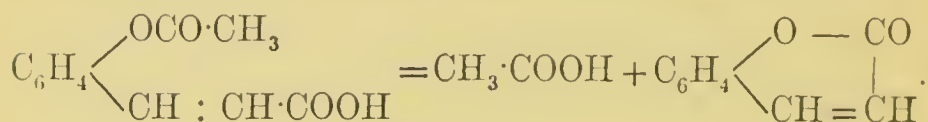
SECTION VII.—AROMATIC ALDEHYDES AND KETONES

61. Preparation of Benzaldehyde $(C_6H_5{\cdot}CHO)$.—Benz-
aldehyde may be obtained in a variety of ways. Thus
benzal chloride is hydrolysed according to the equation,

$$C_6H_5{\cdot}CHCl_2 + H_2O = C_6H_5{\cdot}CHO + 2HCl.$$
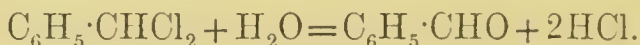
Benzaldehyde may also be prepared from benzyl chloride
by limited oxidation. Nitric acid, as we have already seen,
furnishes benzoic acid. If, however, a solution of copper
nitrate be employed, benzaldehyde is produced:

$$C_6H_5{\cdot}CH_2Cl + O = HCl + C_6H_5{\cdot}CHO.$$

Dissolve 54 grams of copper nitrate in $\frac{1}{2}$ litre of water
contained in a flask of 800–1,000 c.cm. capacity, add
60 grams of benzyl chloride, connect the flask with a reflux
condenser, and boil on the sand-bath for eight hours. At
the end of this time the reaction should be practically
finished. To make certain, allow the liquid to cool; the
oily benzaldehyde should no longer possess the penetrating
smell of the benzyl chloride, and should show only a trace
of chlorine when a clean piece of copper oxide, moistened
with some of the oil, is heated in the bunsen flame.

Separate the benzaldehyde from the aqueous liquid by
extraction with ether. Recover the latter by distilling it
off on the water-bath, and shake the residual oil very
vigorously with an excess of freshly-prepared saturated

solution of acid sodium sulphite. After standing for some time, the sodium bisulphite compound of the benzaldehyde which has separated out may be filtered off with the aid of the pump, washed with very small quantities of water, then with alcohol and ether, and dried on a piece of clean porous earthenware. The crystalline salt, $C_6H_4CH(OH)$ $(SO_3Na), \frac{1}{2}H_2O$, so obtained is then placed in a small flask, covered with dilute sulphuric acid, and distilled in a current of steam. Extract the benzaldehyde from the distillate by ether; dry the ethereal solution over ignited potassium carbonate; remove the ether by distillation on the water-bath; and then distil the benzaldehyde by means of the naked flame.

Colourless liquid with a strong odour of almonds. Boiling point 180°; sp. gr. at 15° 1·0504. Yield from above quantities about 20 grams.

The aromatic aldehydes differ from those of the fatty series (at least the lower members) in not yielding resinous products when treated with alkalies, but undergoing a nearly quantitative reaction whereby equivalent quantities of the corresponding alcohol and acid are produced. Benzaldehyde gives in this way benzyl alcohol and benzoic acid (Cannizzaro's reaction):

$$2C_6H_5CHO + KOH = C_6H_5 \cdot COOK + C_6H_5 \cdot CH_2OH.$$

62. **Preparation of Benzyl Alcohol** ($C_6H_5 \cdot CH_2OH$).—In a small, well-stoppered bottle dissolve 20 grams of stick caustic potash in its own weight of water. When cold add 20 grams of benzaldehyde, and shake the mixture very thoroughly until the emulsion which is formed no longer separates into two layers. Allow the mixture to stand overnight; it will then be found that the contents of the bottle are quite pasty from separation of potassium benzoate.

Dissolve the contents of the bottle in about 100 c.cm. of cold water; this will take up much of the benzyl alcohol in addition to the potassium benzoate. Extract the benzyl alcohol thoroughly by shaking with ether in a separating funnel, separate the ethereal and aqueous solutions, and transfer the former direct to a distilling flask. The ether is first distilled off on the water-bath, the water then removed by heating with the naked flame; after this the thermometer rapidly rises to the boiling point of benzyl alcohol, 204°, which then distils over within two or three degrees. When the thermometer begins to go yet higher, the distillation is stopped, a very small quantity of resinous material being left in the distilling flask.

The yield of benzyl alcohol by this process is about 9 grams.

The potassium benzoate solution left after the extraction with ether should be filtered, raised to boiling, dilute hydrochloric acid added, and allowed to cool. About 11 grams of benzoic acid will be obtained in this manner.

63. **Preparation of Benzoïn** ($C_6H_5 \cdot CH(OH) \cdot CO \cdot C_6H_5$).— Benzaldehyde is readily polymerised in alcoholic solution by potassium cyanide, yielding a ketone-alcohol known as benzoïn :

$$2C_6H_5 \cdot CHO = C_6H_5 \cdot CH(OH) \cdot CO \cdot C_6H_5.$$
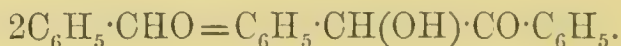
Mix together 45 grams of methylated spirit and 36 grams of water, dissolve in this 2 grams of potassium cyanide and 20 grams of benzaldehyde, and boil the mixture under reflux for $\frac{1}{2}$ hour. The liquid takes on a yellow shade, and, on cooling, the condensation product crystallises out in nearly colourless needles. Filter these off with the aid of the filter pump; transfer the mother liquor once more to the flask; add 1 gram of potassium cyanide; and

boil again for a further 20 minutes.   On cooling, a further crop of benzoïn will be obtained.   Filter off as before, and wash both crops with cold alcohol of the same strength as that stated above.   Press the crystals in a piece of porous earthenware, and recrystallise the product from boiling alcohol.

Colourless crystals, melting at 134°.   Yield about 16 grams.

64. **Preparation of Benzil** ($C_6H_5 \cdot CO \cdot CO \cdot C_6H_5$).—Benzoïn is easily oxidised by moderately strong nitric acid to benzil —diphenyl diketone :

$$C_6H_5 \cdot CH(OH) \cdot CO \cdot C_6H_5 + O = H_2O + C_6H_5 \cdot CO \cdot CO \cdot C_6H_5.$$
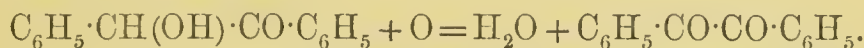
Mix together 20 grams of concentrated nitric acid (sp. gr. 1·42) and 8 grams of water, pour the mixture into a small flask provided with a cork and reflux tube, and then add 12 grams of benzoïn.   Heat the mixture on the water-bath ; the crystals of benzoïn apparently melt and collect on the top of the liquid as a reddish oil, whilst oxides of nitrogen are evolved.   Shake the flask and its contents energetically from time to time, so that the nitric acid has every opportunity of oxidising the benzoïn.   In this case two hours' heating should be sufficient to complete the oxidation.

Pour the product of the reaction into excess of cold water.   The benzil then separates as a yellow crystalline mass ; wash this on the pump with cold water until it is free of nitric acid, and then recrystallise from alcohol.

Yellow crystals, melting point 95°.   Yield 11 grams.

65. **Preparation of Mandelic Nitril and Mandelic Acid** ($C_6H_5 \cdot CH(OH)CN$ and $C_6H_5 \cdot CH(OH) \cdot COOH$).—Although the addition of hydrogen cyanide to aldehydes and ketones has been mentioned, no case of such a reaction has so far

been given. We can, therefore, start with benzaldehyde, act on it with hydrocyanic acid, and convert it thereby into the nitril of mandelic acid, and afterwards hydrolyse this nitril to mandelic acid. The reactions are expressed by the equations,

$$C_6H_5 \cdot CHO + HCN = C_6H_5 \cdot CH(OH) \cdot CN.$$
$$C_6H_5 \cdot CH(OH) \cdot CN + HCl + 2H_2O = C_6H_5 \cdot CH(OH)COOH$$
$$+ NH_4Cl.$$
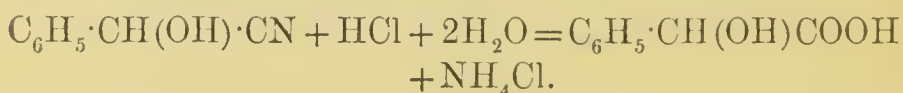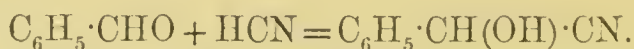
Grind up 15 grams of 96 per cent. potassium cyanide to a fine powder; place this in a small flask, moisten with water slightly, and then add 18 grams of benzaldehyde. Shake the mixture, immerse the flask in a basin containing cold water, and gradually add to the mixture 20 c.cm. of fuming hydrochloric acid (sp. gr. 1·19) which may well be run in from a dropping funnel. The reaction must be performed under a draught cupboard and the flask continually agitated, so that the benzaldehyde, which is not soluble in water, may be brought into reaction with the hydrocyanic acid. When all the hydrochloric acid has been added, allow the mixture to stand for half an hour, and then add water if the mandelic nitril itself is desired. This will then separate as a yellow oil of sp. gr. 1·124, soluble in alcohol and ether, not soluble in water, and not volatile without decomposition.

Since mandelic acid itself is usually required, the nitril can be separated from the aqueous solution by a separating funnel, run off into a flask, and covered with three times its volume of concentrated hydrochloric acid. The reaction which takes place is sufficiently energetic to raise the liquid to boiling. Continue the boiling for an hour by external heating, then transfer the liquid and evaporate first over the naked flame and then on the water-bath to

dryness. Powder the residue, extract the mandelic acid from it with ether, distil off the ether, and recrystallise the mandelic acid from boiling water. Colourless rhombic crystals, melting point 118°.

A method which is to be preferred when one has to deal with large quantities has been described by Dr. Carl Pape (*Chemiker Zeitung*, 1896, **20**, 90), and patented by the Chemische Fabrik vormals Hofmann und Schoetensack in Gernsheim a. Rh. The process consists in adding a concentrated solution of sodium bisulphite (or potassium bisulphite) to commercial benzaldehyde, and shaking the mixture thoroughly. The bisulphite compound of the benzaldehyde which crystallises out is pressed, washed with alcohol, and dried. This is then ground, and mixed to a thin paste with water; a concentrated solution of potassium cyanide is then added, and the mixture stirred. All the bisulphite compound previously undissolved rapidly goes into solution, and the mandelic nitril separates out immediately. The reaction is represented by the equation,

$$C_6H_5 \cdot CH(OH) \cdot SO_3K + KCN = C_6H_5 \cdot CH(OH) \cdot CN + K_2SO_3.$$
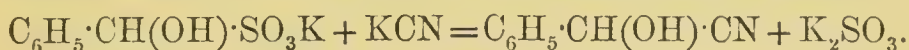
The mandelic nitril is then worked up into mandelic acid in the manner previously described.

66. **Preparation of Salicylic and Parahydroxybenzoic Aldehydes** $\left(C_6H_4 \begin{cases} OH \\ CHO \end{cases} \right)$.—Phenols can be readily converted into aromatic aldehydes by the action of caustic soda and chloroform. When ordinary phenol is treated in this way a mixture of the ortho- and para-hydroxybenzaldehydes is obtained, according to the equation,

$$C_6H_5ONa + 3NaOH + CHCl_3 = C_6H_4 \begin{cases} (1) \ OH \\ (2) \ or \ (4)CHO \end{cases}$$
$$+ 3NaCl + 2H_2O.$$
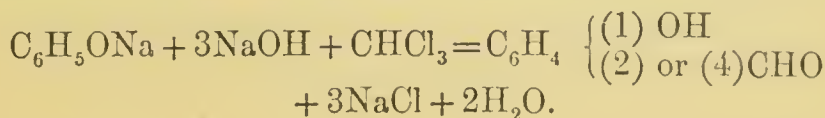
Provide a flask of about $\frac{1}{2}$-litre capacity with a well-fitting cork, through which a long reflux condenser passes. Into this flask pour a solution of 50 grams of phenol dissolved in a solution of 100 grams of caustic soda in 170 c.cm. of water. Now warm the solution to about 55° (thermometer passing through the cork, the bulb being immersed in the liquid) and add in small quantities at a time 75 grams of chloroform. This liquid is introduced by pouring it in at the upper end of the condenser; as it reaches the soda solution of the phenol, reaction immediately sets in, and the liquid rises in temperature. The colour is usually an orange-red by the time all the chloroform has been added. The reaction should be finished by boiling the liquid gently for $1\frac{1}{2}$ hours under reflux. The condenser is then reversed, and the excess of chloroform distilled off on the water-bath. Dilute sulphuric acid is next added until the liquid has a distinctly acid reaction (in order that the aldehydes which are still phenolic in nature may be liberated in the free state from their sodium derivatives), and then subjected to steam distillation as long as salicylic aldehyde is carried over in the current of steam.

The salicylic aldehyde which passes over is, of course, still contaminated with unaltered phenol. Both these substances are extracted by ether from the distillate, most of the ether is distilled off, and the concentrated ethereal solution shaken with a freshly prepared concentrated solution of sodium bisulphite. The addition product of the aldehyde separates out in small colourless leaflets; these are filtered off with the aid of the pump, washed with alcohol, and then added to warm dilute sulphuric acid. The bisulphite compound is thereby decomposed. Extract the liberated salicylic aldehyde with ether, distil off the

ether in the water-bath, and rectify the residue. Colourless liquid, boiling point 196°. Yield 11 grams.

To isolate the parahydroxybenzaldehyde left in the flask after steam blowing, filter the solution whilst still hot through a plaited filter, allow the filtrate to cool, extract with ether, distil off the ether on the water-bath, and recrystallise the residue from boiling water. Colourless needles, melting point 116°. Yield 2 grams.

Section VIII.—Quinones

Quinones may be regarded as a special class of diketones, derived from aromatic compounds by the conversion of two CH groups into carbonyl, or CO, groups. Quinones are either para or, less frequently, ortho, never, however, meta, in the relative positions of their carbonyl groups. Examples of quinones are:
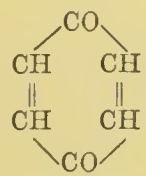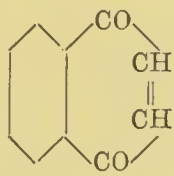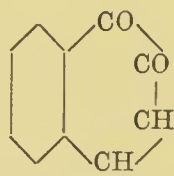
Benzoquinone   α-Naphthaquinone   β-Naphthaquinone
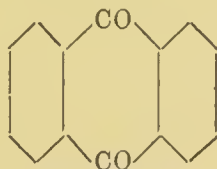
Anthraquinone.

They are produced by the direct oxidation of hydrocarbons, e.g. anthraquinone by the oxidation of anthracene with chromic acid mixture, or by the oxidation of amido-

or hydroxyl-substituted derivatives of the hydrocarbons, as, for example, the production of benzoquinone by the oxidation of aniline.

By reduction the quinones usually pass over into di-hydroxylic phenols; these compounds are, however, easily reoxidised to the quinones from which they have been formed :

$$C_6H_4O_2 + 2H = C_6H_4(OH)_2 \text{ (Hydroquinone)}.$$
$$C_6H_4(OH)_2 + O = C_6H_4O_2 + H_2O.$$
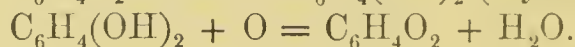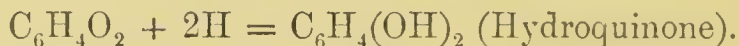
The quinones are reactive substances ; as ketones they combine with one or two molecules of hydroxylamine. The monoxim of benzoquinone is identical with the nitroso-phenol produced by the action of nitrous acid dissolved in sulphuric acid on phenol :

$$C_6H_4O_2 + H_2NOH = C_6H_4O(: NOH) + H_2O.$$
$$C_6H_5(OH) + HONO = C_6H_4(OH)(\cdot NO) + H_2O.$$
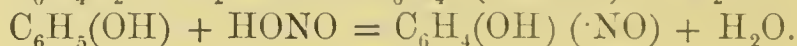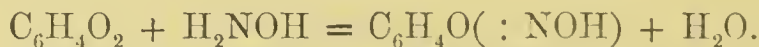
67. Preparation of Benzoquinone $(C_6H_4O_2)$.

Mix together 1 litre of water and 180 c.cm. of concentrated sulphuric acid ; allow the mixture to cool ; pour it into a flask of 3 litres capacity ; dissolve in the dilute solution so prepared 40 c.cm. of aniline ; and then add 200 grams of ice to the contents of the flask. Now add 40 grams of very finely powdered potassium dichromate in quantities of about 1 gram at a time to the mixture, shaking the flask meanwhile, and keeping its contents cooled below 10° by external cooling. The time occupied in adding the bichromate should be about one hour, i.e. allow about ninety seconds to elapse between each addition of a gram of material. In this way the colour will gradually change. Leave the mixture to stand overnight, and next

day proceed to oxidise the dark blackish-violet aniline black which has been produced. This is done by carefully adding a further 80 grams of finely powdered potassium dichromate in small portions at a time, the violet-black colour gradually giving place to a brown shade.

When all the potassium dichromate has been added, allow the mixture to stand for two hours, then extract with 750 c.cm. of ether. Do not shake at all violently during this extraction, as an emulsion is easily formed which will not separate. Repeat the ether extraction with 500 c.cm. of ether; add the two ethereal extracts; dry the solution over calcium chloride; and distil off the ether on the water-bath. The brownish crystalline residue so obtained is nearly equal in weight to the aniline taken; it is pure enough for the preparation of hydroquinone— which may itself be subsequently purified; if a pure preparation of quinone is desired, the crude product should be distilled with steam, the pure compound so obtained will, however, only amount to about 75 per cent. of the crude article.

Quinone forms bright yellow prisms, melting point 116°.

68. **Preparation of Anthraquinone** $\left(C_6H_4 \diagdown{\begin{smallmatrix} CO \\ CO \end{smallmatrix}}\diagup C_6H_4 \right)$.

Finely powder 10 grams of anthracene, which should be as nearly pure as it can be obtained, and dissolve it in a large flask in boiling glacial acetic acid. The flask should be connected with a reflux condenser; if the glacial acetic acid first added is not sufficient to dissolve all the hydrocarbon, add a further quantity through the condenser. When all the anthracene has gone into solution, add

R

gradually through the condenser a solution which has been prepared by dissolving 17 grams of chromic anhydride in a minimal quantity of water, and then adding an equal volume of glacial acetic acid.   After all the chromic acid has been added, the heating is continued until the solution has assumed a deep green tint ; the solution is then poured out into a large excess of water.   The anthraquinone is thus precipitated as a fine yellow powder, which, after standing some hours, is filtered off, washed with boiling water, hot dilute caustic soda solution, and then again with hot water.   After drying, the anthraquinone is purified by sublimation.

Yellow rhombic prisms.   Melting point 277°, boiling point 378°.

When anthraquinone is sulphonated, it is first converted into anthraquinone β-sulphonic acid.   The constitution of this acid is expressed by the formula :
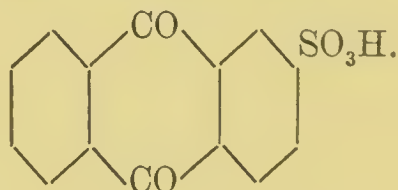
On fusion of the sodium salt of this acid with caustic soda, the sulphonic group is replaced by hydroxyl ; oxidation takes place simultaneously (to promote this a chlorate may be added) and alizarine is produced :

$+ 3NaOH + O$

$$= \text{[structure: CO, ONa, ONa, CO]} \quad + \text{Na}_2\text{SO}_3 + 2\text{H}_2\text{O}.$$
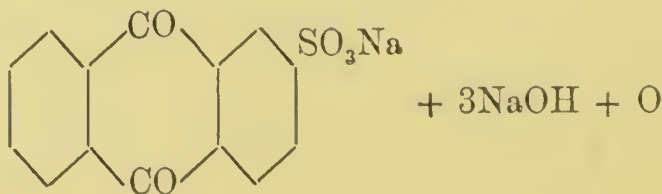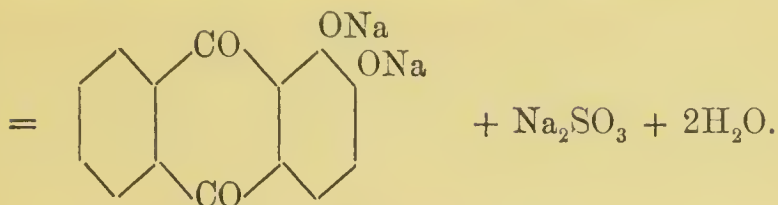
69. Preparation of Nitroso-β-Naphthol [1] (β-naphtha quinone a-oxim $C_{10}H_6O$ (: NOH)).

It has already been mentioned that when phenol is treated with nitrous acid the oxim of benzoquinone is produced. In a similar manner nitrous acid reacts with β-naphthol to form the a-oxim of β-naphthaquinone :

$$\text{[structure: OH]} + \text{HNO}_2 = \text{[structure: NOH, O]} + \text{H}_2\text{O}.$$
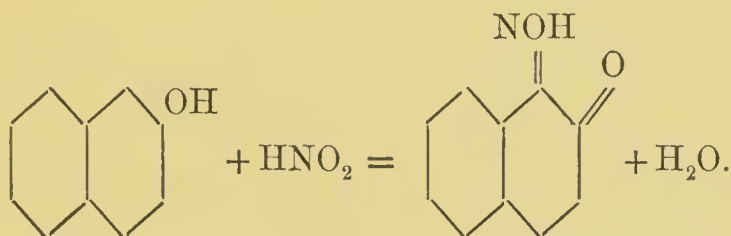
The reaction is brought about by using zinc chloride instead of hydrogen chloride in conjunction with the alkaline nitrite, the zinc salt of nitrosonaphthol being produced. Connect a flask of $\frac{1}{2}$- to $\frac{3}{4}$-litre capacity with a reflux condenser, and in it dissolve 40 grams of β-naphthol and 30 grams of zinc chloride in 250 c.cm. of alcohol. Run into the boiling solution 40 c.cm. of a strong solution of sodium nitrite (one part sodium nitrite to two parts water) in a thin stream. The liquid soon becomes red, and after boiling a short time the zinc salt of nitroso-β-naphthol begins to crystallise out. Then discontinue the boiling, allow the liquid to stand overnight, and then filter off the salt which has separated, and wash it with alcohol.

[1] The sodium salt of this compound is used as a dye-stuff ; it is the Gambine Y of Holliday & Sons (Huddersfield).

Now grind up the zinc salt with 400 c.cm. water, and after adding a solution of 36 grams of caustic soda in 80 c.cm. water, warm on the water-bath, stirring the mixture until the solid matter has been converted into the green crystalline sodium salt. Allow the liquid to cool, filter off the sodium salt with the aid of the pump, wash it with a small quantity of water, transfer to a beaker, and decompose the salt with 30–40 c.cm. of concentrated hydrochloric acid diluted with twice its volume of water. Filter off, wash with cold water, and recrystallise from alcohol.

Yellowish crystals, melting point 109·5°. Yield about 40 grams.

Section IX.—Condensations resulting in the Formation of Closed Ring Compounds

In addition to closed ring compounds of the type of benzene, naphthalene, &c., many other compounds are known in which other atoms besides carbon play a part in the formation of closed chains. Very nearly related to benzene, naphthalene, and anthracene, are the nitrogenous compounds pyridine, C_5H_5N, quinoline, C_9H_7N, and acridine, $C_{13}H_9N$, each of which may be regarded as derived from the hydrocarbons mentioned by replacement of a methenyl (CH) group by a nitrogen atom. This is at once rendered evident from their constitutional formulæ :—
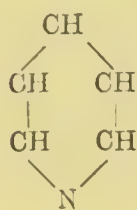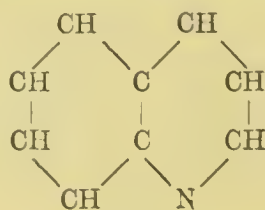
Pyridine   Quinoline   Acridine.
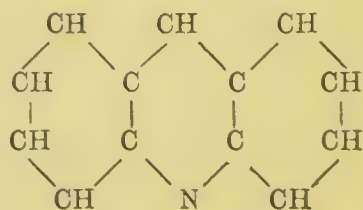
Many derivatives of these compounds may be produced by synthetical methods.

70. Hantzsch's Synthesis of Ethyl Collidinedicarboxylate,

$$\begin{array}{c} \text{C·CH}_3 \\ \text{CO}_2\text{C}_2\text{H}_5\text{·C} \diagup\diagdown \text{C·CO}_2\text{C}_2\text{H}_5 \\ | \quad\quad | \\ \text{CH}_3\text{·C}\diagdown\diagup\text{C·CH}_3 \\ \text{N} \end{array}$$
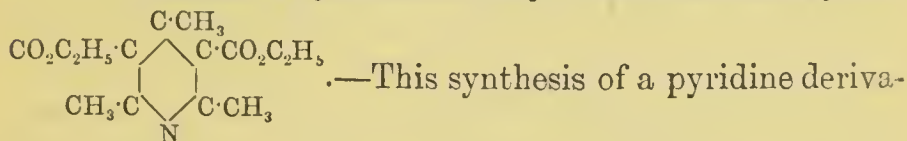
.—This synthesis of a pyridine deriva-

tive consists in first condensing acetoacetic ether—a compound frequently used for closed ring condensations— with aldehyde-ammonia. These two substances then form the dihydro-derivative of the above-named ester as follows :—

$$\underset{\underset{\text{CH}_3\text{·C(OH)}}{\parallel}}{\text{C}_2\text{H}_5\text{OOC·CH}} \quad + \quad \underset{\underset{\text{NH}_3}{}}{\overset{\overset{\text{CH}_3}{|}}{\underset{}{\text{CHO}}}} \quad + \quad \underset{\underset{\text{(HO)C·CH}_3}{\parallel}}{\text{HC·COOC}_2\text{H}_5}$$

$$= \underset{\underset{\text{CH}_3\text{·C}}{\parallel}}{\text{C}_2\text{H}_5\text{OOC·C}} \overset{\overset{\overset{\text{CH}_3}{|}}{\text{CH}}}{\diagup\diagdown} \underset{\underset{\text{NH}}{}}{\underset{\underset{\text{C·CH}_3}{\parallel}}{\text{C·COOC}_2\text{H}_5}} \quad + \quad 3\text{H}_2\text{O}.$$
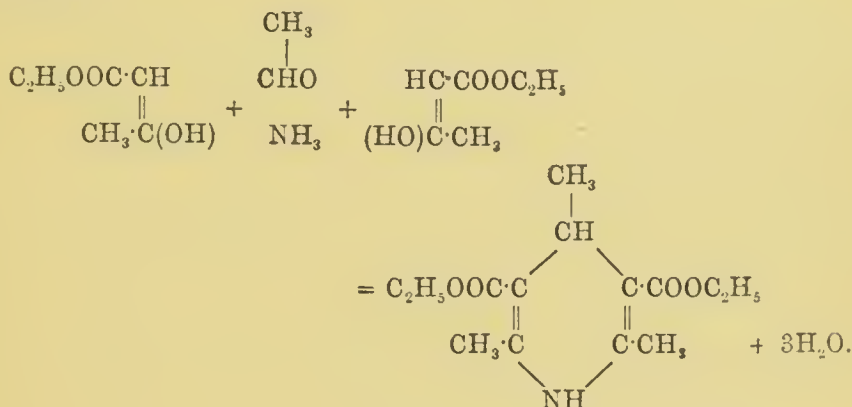
When this diethyl dihydrocollidinedicarboxylate is treated in alcoholic solution with nitrous acid, two atoms of hydrogen are oxidised off and the true pyridine derivative is formed :

$$\text{C}_5\text{H}_2(\text{CH}_3)_3(\text{COOC}_2\text{H}_5)_2 + \text{O} = \text{C}_5(\text{CH}_3)_3(\text{COOC}_2\text{H}_5)_2 + \text{H}_2\text{O}.$$
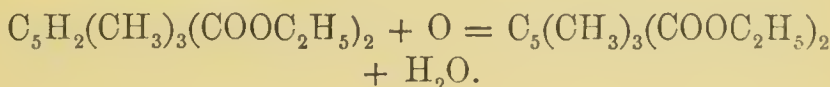
Weigh out into a small beaker or a boiling tube 30 grams of acetoacetic ether and 8 grams of aldehyde-ammonia ; a clear solution is first obtained, but on warming, drops of water begin to separate. The source of heat is then

removed, since on account of the heat evolved by the reaction the liquid continues to boil gently by itself. When boiling ceases, the flame is again applied, and the liquid boiled gently for four or five minutes, being thoroughly stirred during this part of the process. The still warm mass is now treated with hot alcohol until clear, and allowed to cool; the crystals are then filtered off on the pump, and washed with water. The alcoholic mother liquors deposit more of the substance if allowed to stand; this is impure, and should be recrystallised from boiling alcohol.

Ethyl dihydrocollidinedicarboxylate forms colourless tablets, melting at 131°. The yield with the above-named quantities should be about 20 to 21 grams. Now arrange the apparatus for the oxidation of the dihydro ester with nitrogen trioxide. A is a flask in which 55 grams of arsenic trioxide are acted on with an equal weight of strong nitric acid [1] (sp. gr. 1·42). B is an empty washing bottle, cooled by immersion in water, which serves to hold back any nitric acid carried over by the nitrogen trioxide. In C 15 grams of the ethyl dihydrocollidinedicarboxylate is mixed with its own weight of alcohol, and kept cool by immersion of the flask in water. By gently warming the contents of A from time to time, gas is evolved, which, evolving heat with the contents of C, soon brings everything into solution. As soon as a small specimen of the

[1] The quantities taken are in excess of those required; but since arsenic acid will be needed for the next preparation, it is as well to take sufficient arsenic trioxide and nitric acid to make 75 to 80 grams of arsenic acid. When all the ethyl dihydrocollidinedicarboxylate has been oxidised, continue to heat the contents of A until the oxidation of the arsenic is complete. Then transfer the contents to a platinum dish, and evaporate until the mass completely solidifies on cooling. Powder, and keep in a well-stoppered bottle for use.

liquid in c dissolves completely in dilute hydrochloric acid, the liquid is poured out into an evaporating basin, the alcohol evaporated off with the help of the water-bath, and dilute solution of caustic soda added until the reaction is distinctly alkaline. The oxidised ester which thereby separates is extracted by ether in a separating funnel, the ethereal solution dried over ignited potassium carbonate,
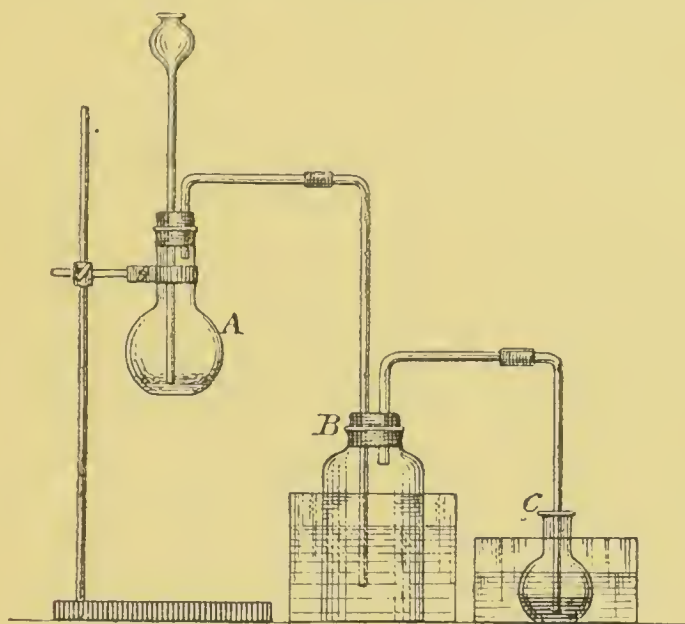
Fig. 63.

and then distilled, the ether being removed on the water-bath. Ethyl collidinedicarboxylate passes over as a yellowish oil, boiling at 308°–310°. The amount obtained should be 11 to 12 grams.

71. **Preparation of Quinoline** (C_9H_7N).—Into a large flask provided with a long reflux condenser introduce a mixture of 76 grams of arsenic acid (*see* last preparation), 145 grams of concentrated sulphuric acid, 155 grams of glycerine, and 50 grams of aniline. Heat the mixture

slowly on a sand-bath, shaking the contents of the flask thoroughly from time to time until reaction sets in. Then remove the flame if the reaction is at all violent,[1] and after the first reaction is over, keep the liquid in the flask gently boiling for $2\frac{1}{2}$ hours. The reaction which takes place may be represented by the equation,

$$2C_6H_5NH_2 + 2C_3H_8O_3 + 2H_3AsO_4 = 2C_9H_7N + 11H_2O + As_2O_3.$$
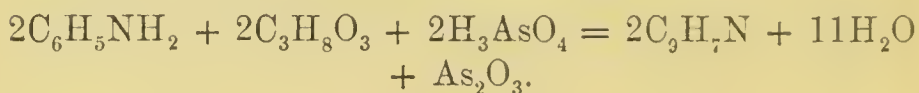
Allow to cool somewhat, dilute with water, and add caustic soda until the liquid has a distinctly alkaline reaction. Then remove the quinoline and any unattacked aniline in a current of steam, receiving the distillate in a large beaker. Add hydrochloric acid in excess to the distillate, so that a clear solution is obtained, and now pour in a solution of sodium or potassium nitrite until the smell of nitrous acid is permanent. Then blow steam through the solution until all the diazonium salt is destroyed, add caustic soda in excess, and once more steam distil the liquid until all the quinoline has been blown over. Separate the quinoline in the distillate as completely as possible from the aqueous portion by a separating funnel; extract the latter with ether; add the ethereal extract to the other portion of the quinoline; dehydrate the ethereal solution with stick caustic potash; and subject to distillation. The quinoline passes over as a practically colourless oily basic liquid of boiling point 236°. Yield 46 grams.

The synthesis of quinoline from aniline has been effected in various ways. In 1881, Königs described its prepara-

---

[1] Usually the reaction proceeds very quietly in the conversion of aniline into quinoline. The difference between this method and Skraup's is soon appreciated by those who have tried both.

tion by leading the vapour of allylaniline over red-hot lead oxide :—

$$C_6H_5 \cdot NH \cdot CH_2 \cdot CH : CH_2 + 2PbO = 2Pb + 2H_2O$$

$$+ \ C_6H_4 \underset{N}{\overset{CH}{<}} \overset{CH}{\underset{CH.}{|}}$$

Skraup prepared it soon after by the dry distillation of acroleïn-aniline :

$$C_6H_5 \cdot N : CH \cdot CH : CH_2 = C_6H_4 \underset{N \ = \ CH}{\overset{CH \ = \ CH}{<}} \ + \ H_2.$$

He then modified his process by adding glycerine and sulphuric acid to aniline itself, and heating the mixture ; but soon made another change in adding nitrobenzene. The reaction must then be formulated :—

$$2C_6H_5NH_2 + C_6H_5NO_2 + 3C_3H_8O_3 = 3C_9H_7N + 11H_2O.$$

The method above described in which arsenic acid is used as an oxidising agent is due to Knueppel (*Berichte*, 1896, **29**, 703). By this process the yields obtained are usually better, and the reaction goes less violently.

72. **Preparation of Methyl-Uracil**

$$\left(\ H \cdot C \underset{CO \ - \ NH}{\overset{CH_3 \cdot C \ - \ NH}{<}} CO \ \right).$$—Grind up in a small mortar

to a fine powder 10 grams of urea ; mix this with 20 grams of acetoacetic ether, 40 c.cm. of alcohol, and 5 drops of concentrated hydrochloric acid. Cork up the mixture in a small flask, and allow it to stand there for about a week. Then pour the mixture into an evaporating

basin, and allow the liquid to evaporate in a vacuum desiccator over strong sulphuric acid until the mass contained in the basin is quite dry. The ethyl uramido-crotonate thus obtained has been produced according to the equation :

$$
\underset{\substack{\| \\ \text{CH} \\ | \\ \text{COOC}_2\text{H}_5}}{\text{CH}_3\text{·C(OH)}} + \text{H}_2\text{N·CO·NH}_2 = \text{H}_2\text{O} + \underset{\substack{\| \\ \text{CH} \\ | \\ \text{COOC}_2\text{H}_5.}}{\text{CH}_3\text{·C·NH·CO·NH}_2}
$$
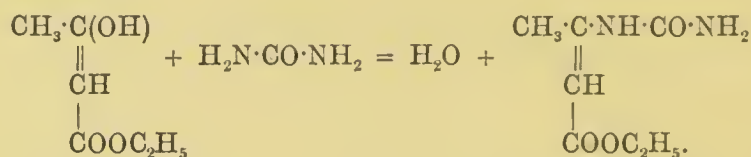
This has next to be converted into the corresponding sodium salt. Dissolve the ester in a minimum quantity of absolute alcohol, and add to the solution sodium ethylate dissolved in alcohol in the proportion of equal molecules. (For every 172 parts by weight of uramido-crotonic ester dissolve 23 parts by weight of sodium in 10 times its weight of alcohol). On mixing the two alcoholic solutions, the sodium salt separates out immediately as small colourless needles, the hydrolysis of the ethyl ester taking place with great rapidity. To liberate the methyluracil from the sodium salt, dissolve it in water, in which it is very easily soluble, and then saturate the solution with carbon dioxide. The sodium salt is thereby decomposed ; but the free uramido-crotonic acid is not obtained ; internal anhydridisation takes place, and methyluracil is precipitated :

$$
2\;\underset{\substack{\diagdown \\ \text{COONa}\;\text{NH}_2}}{\overset{\substack{\text{CH}_3\text{·C—NH} \\ \diagup\;\diagdown}}{\text{HC}\qquad\text{CO}}} + \text{CO}_2 = \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \underset{\substack{\diagdown \\ \text{CO—NH}}}{\overset{\substack{\text{CH}_3\text{·C—NH} \\ \diagup\;\diagdown}}{\text{H·C}\qquad\text{CO.}}}
$$
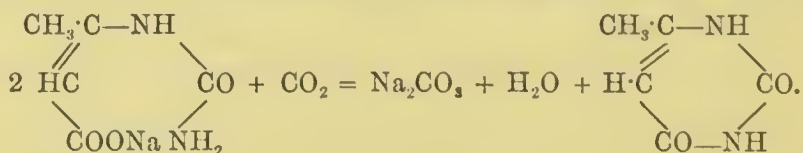
By recrystallisation from alcohol, the methyluracil can be obtained as colourless needles ; on heating, these do not melt, but decompose about 270°–280°.

Methyluracil is of great interest, as it was made use of

by Behrend to effect the synthesis of uric acid (Behrend and Roosen, *Annalen*, **251**, 235). If methyluracil be acted on by fuming nitric acid (adding 4 grams of methyluracil to 10 c.cm. of the acid, sp. gr. 1·5), nitrouracilcarboxylic acid is produced. By heating the potassium salt of this compound to 130°, carbon dioxide is expelled and the potassium salt of nitrouracil obtained:

$$\begin{array}{ccc}
\text{HO}_2\text{C·C} - \text{NH} & & \text{CH} - \text{NH} \\
\quad\;\; \text{//} \qquad\quad \text{\textbackslash} & & \quad \text{//} \qquad\quad \text{\textbackslash} \\
\text{NO}_2\text{·C} \qquad\quad \text{CO} = \text{CO}_2 + \text{NO}_2\text{·C} \qquad\quad \text{CO.} \\
\quad\; \text{\textbackslash} \qquad\quad \text{/} & & \quad \text{\textbackslash} \qquad\quad \text{/} \\
\text{CO} - \text{NH} & & \text{CO} - \text{NH}
\end{array}$$
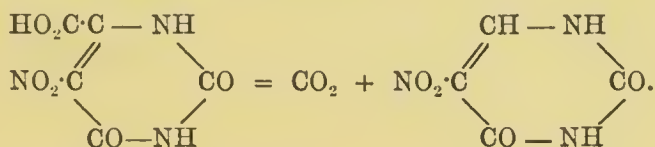
When nitrouracil is reduced by tin and hydrochloric acid, amido- and hydroxy-uracils are obtained, the former soluble in hydrochloric acid, the latter insoluble. The latter is easily oxidised by bromine water to a dihydroxy-uracil as follows:

$$\begin{array}{ccc}
\text{H·C} - \text{NH} & & \text{HO·C} - \text{NH} \\
\text{//} \qquad\quad \text{\textbackslash} & & \quad \text{//} \qquad\quad \text{\textbackslash} \\
\text{HO·C} \qquad\quad \text{CO} + \text{Br}_2 + \text{H}_2\text{O} = 2\text{HBr} + \text{HO·C} \qquad\quad \text{CO.} \\
\text{\textbackslash} \qquad\quad \text{/} & & \quad \text{\textbackslash} \qquad\quad \text{/} \\
\text{CO} - \text{NH} & & \text{CO} - \text{NH}
\end{array}$$
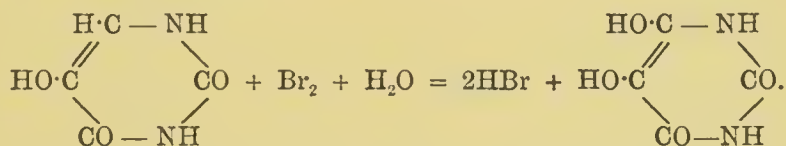
Finally, when this compound is warmed with urea and sulphuric acid, uric acid is produced:

$$\begin{array}{ccc}
 & \text{HO·C} - \text{NH} & \\
\qquad \text{NH}_2 & \quad \text{||} \quad\; \text{|} & \quad \text{NH} - \text{C} - \text{NH} \\
\text{CO} \qquad\quad + \text{HO·C} \quad \text{CO} = 2\text{H}_2\text{O} + \text{CO} \qquad\quad \text{||} \quad\; \text{|} \\
\qquad \text{NH}_2 & \quad \text{|} \qquad\; \text{|} & \quad \text{NH} - \text{C} \quad \text{CO} \\
 & \text{CO} - \text{NH} & \quad\; \text{|} \qquad\; \text{|} \\
 & & \quad \text{CO} - \text{NH.}
\end{array}$$
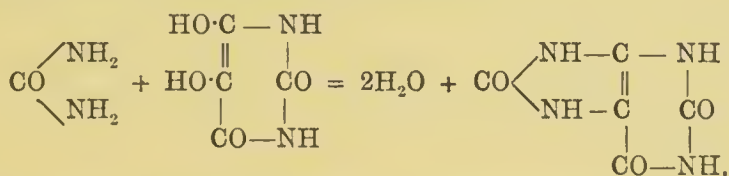
73. Preparation of Phenylmethylpyrazolone

$$\left(\begin{array}{c}
\text{CH}_3\text{·C} - \text{CH}_2 \\
\quad \text{||} \qquad\quad \text{|} \\
\quad \text{N} \qquad \text{CO} \\
\quad \text{\textbackslash} \qquad \text{/} \\
\quad\;\; \text{N·C}_6\text{H}_5
\end{array}\right)\text{.—Phenylhydrazine reacts readily with}$$
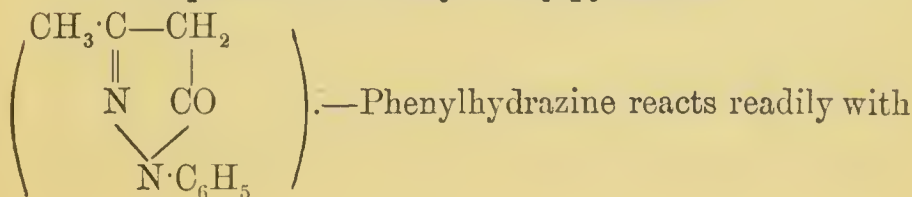
β-ketonic acids (or usually their esters), first forming a hydrazone and then a pyrazolone derivative by further loss of water. The two reactions may be expressed by the general reactions:

$$
\text{(i)} \quad
\begin{array}{c}
\text{R·CO} \\
| \\
\text{CH}_2 \\
| \\
\text{COO·Alk}
\end{array}
\quad \text{H}_2\text{N·NH·C}_6\text{H}_5 \quad
= \text{H}_2\text{O} +
\begin{array}{c}
\text{R·C}=\text{N·NH·C}_6\text{H}_5 \\
| \\
\text{CH}_2 \\
| \\
\text{COO·Alk.}
\end{array}
$$

$$
\text{(ii)} \quad
\begin{array}{c}
\text{R·C}=\text{N·NH·C}_6\text{H}_5· \\
| \\
\text{CH}_2 \\
| \\
\text{COO·Alk}
\end{array}
\quad = \text{Alk·OH} +
\begin{array}{c}
\text{R·C}=\text{N} \\
| \qquad | \\
\text{CH}_2 \quad \text{N·C}_6\text{H}_5. \\
\diagdown \quad \diagup \\
\text{CO}
\end{array}
$$
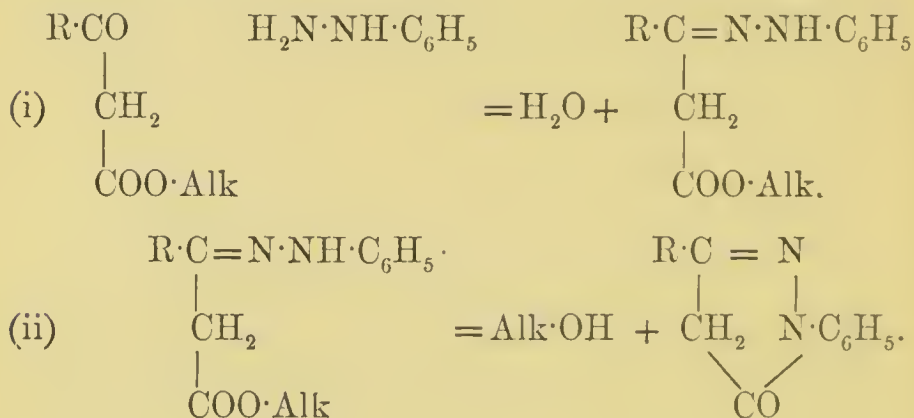
Mix intimately together in a small beaker 20 grams of phenylhydrazine and 25 grams of acetoacetic ester. The mixture becomes warm, and drops of water separate out from the liquid, the first stage of the condensation, resulting in the formation of the phenylhydrazone, taking place without any external application of heat. Transfer the beaker to a water-bath, stir the contents well with a glass rod whilst the liquid is being heated; the water will soon evaporate, and under the influence of the heat the second stage of the reaction, resulting in the formation of the pyrazolone derivative, takes place. This is known by the liquid in the beaker becoming very viscous and finally pasty, at the end of 2 to 2½ hours; remove the mass whilst still warm from the beaker to another beaker containing about 50 to 100 c.cm. of ether. The phenylmethylpyrazolone sets immediately to a nearly colourless hard solid mass. Pour off the discoloured ethereal solution; wash the residue twice by decantation with small quantities

of ether; press the mass on porous earthenware; and re-
crystallise from boiling alcohol. The phenylmethylpyra-
zolone will be thus obtained in colourless needles, melting
at 127°.

When phenylmethylpyrazolone is heated to 100°–120°
under pressure with caustic potash, methyl iodide, and
methyl alcohol, a phenyldimethylpyrazolone is produced,
methyl iodide being apparently first added, and then the
elements of hydriodic acid removed :

$$
\begin{array}{ccc}
\begin{array}{c}
\mathrm{CH_3 \cdot C\!\!-\!\!-\!\!CH_2} \\
\parallel \quad\ \ | \\
\mathrm{N \quad\ CO} \\
\diagdown\ \diagup \\
\mathrm{N(C_6H_5)}
\end{array}
&
+\ \mathrm{CH_3I}\ =
&
\begin{array}{c}
\overset{\displaystyle \mathrm{I}}{\underset{}{|}} \\
\mathrm{CH_3 \cdot C\!\!-\!\!-\!\!CH_2} \\
|\qquad\ \ | \\
\mathrm{CH_3 \cdot N \quad CO} \\
\diagdown\ \diagup \\
\mathrm{N(C_6H_5)}.
\end{array}
\end{array}
$$

$$
\begin{array}{ccc}
\begin{array}{c}
\overset{\displaystyle \mathrm{I}}{\underset{}{|}} \\
\mathrm{CH_3 \cdot C\!\!-\!\!-\!\!CH_2} \\
|\qquad\ \ | \\
\mathrm{CH_3 \cdot N \quad CO} \\
\diagdown\ \diagup \\
\mathrm{N(C_6H_5)}
\end{array}
&
=\ \mathrm{HI}\ +
&
\begin{array}{c}
\mathrm{CH_3 \cdot C\ =\ CH} \\
|\qquad\ \ | \\
\mathrm{CH_3 \cdot N \quad CO} \\
\diagdown\ \diagup \\
\mathrm{N(C_6H_5)}.
\end{array}
\end{array}
$$
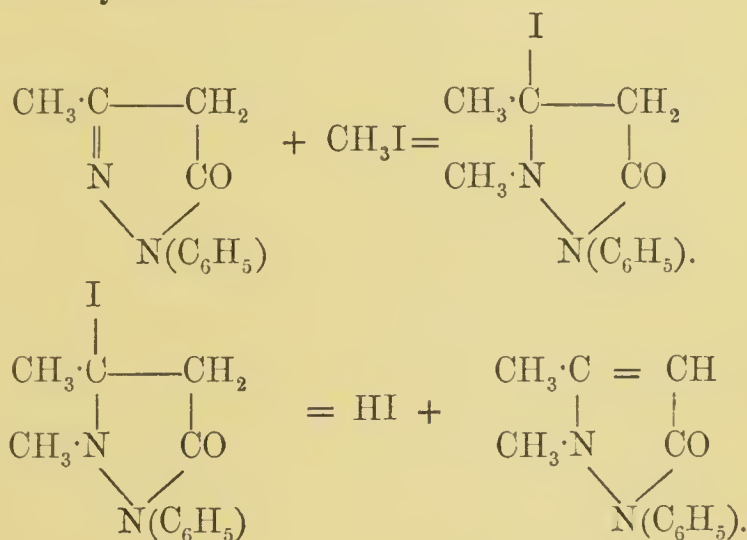
This phenyldimethylpyrazolone forms the drug known
as antipyrine.

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